STUDIES ON THE DEGRADATION OF INDUSTRIAL WASTE WATER USING HETEROGENEOUS PHOTOCATALYSIS

A Dissertation
Submitted in partial fulfillment of the requirements for the award of degree

MASTER OF TECHNOLOGY
IN
ENVIRONMENTAL SCIENCES AND TECHNOLOGY

By
Manmohan lal kamboj
(Regn. No.-60701003)

Under the Guidance of
Mr. Amit Dhir
(Lecturer, Department of Biotechnology & Environmental Sciences)

DEPARTMENT OF BIOTECHNOLOGY & ENVIRONMENTALSCIENCES,
THAPAR UNIVERSITY
PATIALA-147004 (PUNJAB)

JUNE-2009

Date: ______________

DECLARATION

I hereby declare that the work embodied in dissertation entitled **"Studies on the degradation of industrial wastewater using heterogeneous photocatalysis"** 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.

MANMOHAN LAL
(REGN.NO.-60701003)

DEPARTMENT OF BIOTECHONOLOGY AND ENVIRONMENTAL SCIENCES,
THAPAR UNIVERSITY, PATIALA-147004 [PUNJAB]

Date: 8/7/09

CERTIFICATE

This is to certify that the dissertation entitled, **"Studies on the degradation of industrial wastewater using heterogeneous photocatalysis"**, is an authentic work carried out by Manmohan Lal 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.

Dhir

Amit Dhir
Lecturer, (Department of Biotech. & Env. Sc.)
Thapar University, Patiala

08/07/2009

Head
(Department of Biotech. & Env. Sc.)
Thapar University, Patiala

RK Sharma
13/7/09

Dean
(Academic Affairs)
Thapar University, Patiala

It is matter of immense pleasure to acknowledge my debt to my revered teacher and Supervisor **Mr. Amit Dhir,** Lecturer, Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. It is because of his priceless intellectual guidance, innovative and constructive ideas for having given me complete independence, affectionate encouragement to put my desire and thought, which paved the way for the successful completion on this seminar. It is indeed my privilege to work under him. I express my special regards to **Dr. Niranjan Das,** Assistant Professor and Head, Department of Biotechnology and Environmental Sciences, Thapar University, Patiala for his ever-helping attitude during the course of this project work.

I can not forget to express my warmest thanks to **Dr. Anita Rajor and Mr. Ashwani Agarwal** for their round the clock help and cooperation. I am also thankful to teaching and non teaching staff members of the department for their invaluable cooperation and help during the entire tenure of my studies in the department.

I take this opportunity to thank all my friends especially Somdutt Yadav, , Chhotu Ram, Sumit Rana, Isha, Narotam Garg, Manjeet Kumar, Sampurnanand Singh, Vidhu Triphati, Ravi Pareek, Vinod , Hemant, Rishi, Nagesh, P. K Goyal for their help and moral support.

Last, but not least, I thank **God** for giving me strength to overcome difficulty, which crossed my way to be a pole star.

Thank you for making this a reality.

Manmohan Lal Kamboj

ABSTRACT

The release of wastewater into the receiving water bodies is deleterious, not only because of their color, but also because they are not easily degraded by aerobic bacteria and forms toxic compounds under the action of anaerobic bacteria. Therefore, it becomes imperative to completely degrade these organic compounds before their discharge. Such pollutants cannot be completely degraded by well established techniques like coagulation, flocculation, precipitation, adsorption, membrane separation, aerobic biological treatment. The incapability of conventional wastewater treatment methods to effectively remove such pollutants leads to explore the new, efficient and cost effective treatment systems. In order to meet stringent environmental regulations, the latest development is the oxidation of these biorecalcitrant organic compounds. These radicals have high oxidizing power superior to other usual oxidants and results in complete degradation. The methods are called advanced oxidation processes (AOP's). AOP's include homogenous and heterogeneous photocatalytic processes, however the latter being more promising technique for the degradation of industrial effluent. Photocatalytic process relies on the activation of semiconductor resulting in the generation of electrons and holes which results in series of redox reaction to destroy the pollutants. TiO_2 has been demonstrated to be excellent catalyst and its behavior is well documented in the literature.

Although the strong potential of photocatalytic process for wastewater treatment is widely recognized but its technical development at industrial scale is not met with much success due to its high operating cost. Taking all these facts into consideration, in the present study, effluent was collected from Chemical & Pharmaceutical industry from Punjab region. Photo degradation of effluent was performed in specially designed reaction vessel in the photoreactor equipped with UV tubes and constant stirring of solution was ensured at constant temperature. Experiments were performed in slurry mode in both UV and solar light at optimized condition. The degradation of effluent has been investigated in terms of change in reduction in COD and solid content. Various process parameters like catalyst dose, pH, concentration of oxidant, initially pollutant concentration were varied and their effects have been analyzed.

In the case of Chemical and Pharmaceutical effluent, TiO_2 dose was optimized to be 3.0mg/l, at operating pH of 4.0 along with oxidant concentration of 250ml/l at UV intensity of 25 W/m^2.

So, heterogeneous photocatalytsis can be used as efficient and environmental friendly technique for the complete degradation of recalcitrant compound present in effluent 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.

The treatment of chemical pharmaceutical effluent result in the COD reduction from 8000 mg/l to 80 mg/l & 350 mg/l in UV and Solar light respectively after 7 hrs of treatment under optimized condition. The result shows degradation of effluent of the order of 99% and 95% in UV & Solar light respectively. The tests on solid analysis depicts reduction of TDS from 1270 mg/l to 350 mg/l & 390 mg/l in UV & Solar light respectively. Hence it is evident that the result in solar light are comparable with the result obtained in UV light, hence solar light can be suitable and effectively used as a light source for photodegradation.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER-1

INTRODUCTION

Water is basic requirement in all industrial processes, domestic and commercial activities, so the wastewater generated from these various processes contains various contaminants depending upon process, mainly pharmaceutical, textile, acrylic Fiber, pesticides and other organic chemicals manufacturing industries etc. generate waste water containing phenolic compounds and various dyes. These effluents are intensely colored and are contaminated with high concentration of organic compounds such as suspended and dissolved salts and many other recalcitrant compounds. Even small concentration of these compounds present in effluent causes toxicity and foul odors to water. If these effluents are improperly treated, they will pose to serious threat to all species on earth because hydrolysis of the pollutants in waste water can produce a great deal of toxic products. Degradation of these non-biodegradable organic compounds is not possible by conventional biological treatment processes. Lately, there has been a lot of interest in application of the advanced oxidation processes (AOP's) for the removal of these organic compounds. Many processes such as photolysis, photo catalytic oxidation, ozonation, Fenton oxidation, wet air oxidation and membrane separation has been proposed for the degradation of these compounds even at low concentration *(Naresh N. Mahamuni et al., 2005 ; Jun Wang et al., 2005).*

1.1 Problems Associated With Industrial Waste Water

One of the characteristics that best define today's society in what is understood as developed countries is the production of waste products. There is practically no human activity that does not produce waste products and in addition there is a direct relationship between the standard of living in a society or country and the amount of waste products produced. Approximately 23% of the world's population live in developed countries, consume 78% of the resources and produce 82% of the waste products. In addition, it has to be pointed out that the volume of residual waste increases in an exceptional way with regards to a country's level of industrialization. At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide, and it is estimated that 1,000 new chemical substances are added to the list each year.

Large contrasts are reflected in the problems related to the rational management of water, which cannot be dealt with in a unilateral way, but by many different procedures. A publication describes in a generic form the problems that societies have had to face regarding water use as the society evolved. The countries with sustainable development have, one by one, confronted the problems related to biological contamination, with the levels of heavy metals, with the intensive use of nutrients, and with organic contaminants at very low levels. Water disinfections, the treatment of effluents before being discharged into water systems, the limitation and substitution of nitrates and phosphates in products that are used on a massive scale and the development in analytical chemistry and in ecotoxicology are examples of some of the "tools" used to combat these problems. It must be noted that the time scale to resolve each problem as it arises, is always shorter. The problems derived from the toxicological effects of organic compounds, which are active at very low levels, must be resolved at the same time as water disinfection for rural communities. It is clear that innovative procedures are needed to deal with this wide range of problems, which vary notably in its application scale and the complexity of the problems.

Relatively recently, the discharging of waste in the environment was the way of eliminating them, until the auto-purifying capacity of the environment was not sufficient. The main problem stems from waste coming from industry, despite the fact that the population also plays an important role in environmental contamination. Phenols, pesticides, fertilizers, detergents, and other chemical products are disposed of directly into the environment, without being treated, via discharging, controlled or uncontrolled and without a treatment strategy. In this general context, it is very clear that the strategy to continue in the search of solutions to this problem that every day presents a sensitive growth, mainly in the developing countries, it will be guided by two fundamental aspects:

- The development of appropriate methods for contaminated drinking, ground, and surfaces waters
- The development of appropriate methods for wastewaters containing toxic or non-biodegradable compounds.

The European Union made out a list of dangerous compounds, considered as contaminants, to which constantly new substances are added (“black list” of the E.U., see Table 1.1). The presence of this type of pollutant in an aqueous dissolution is especially problematic as the residual waste cannot be stored indefinitely (as is the case with some solid waste) and it has the peculiarity that a small volume of water is able to contaminate much greater volumes of water. It must also be pointed out that a wide spectrum of compounds can transform themselves into potentially dangerous substances during the drinking water treatment process, particularly by chlorination, as is the case of the precursor compounds of the formation of chlorocarbons.

Table 1.1 Black lists of chemicals substances selected by the E.U. (Harrinson, 1992)

Group	Included substances
Chloride Hydrocarbons	Aldrin,dieldrin,chlorobenzene,dichlorobenzene,chloronaphthalene, chloroprene,chloropropene,chlorotoluene,endosulfane,endrin, hexachlorobenzene,hexachlorobutadiene,Hexachlorocyclo-hexane, hexachloroethane, PCBs, tetrachlorobenzene, trichlorobenzene.
Chlorophenol	Monochlorophenol,2,4-dichlorophenol,2-amino-4-chlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, trichlorophenol.
Pesticides	Cyanide chloride, 2,4-dichlorophenoxyacetic acid and derivatives, 2,4,5 trichlorophenoxyacetic acid and derivatives, DDT, demeton, dichloroprope, dichlorvos,dimethoate,disulfoton,phenitrothion,phenthyon,linuron,malathion, MCPA, mecoprope, monolinuron, omethoate, parathion, phoxime, propanyl, pirazone, simacine, triazofos, trichlorofon, trifularin and derivatives.
Chloroanilines and nitro benzenes	Monochloroanilines, 1-chloro-2,4 dinitrobenzene, dichloroaniline, 4-chloro-2-nitrobenzene,chloronitrobenzene,chloronitrotoluene, dichloronitrobenzene.
Polycyclic Aromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Inorganic substances	Arsenic and its compounds, cadmium and its compounds, mercury and its compounds.
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene,dichloromethane,dichloropropane,dichloropropanol,dichloropropene,ethylbenzene,toluene,tetrachloroethylene,trichloroethane, trichloroethylene.

1.2 Physical Characteristics

The most important physical characteristics of wastewater is total solids content which is composed of floating matter settable matter, colloidal matter and matter in solution important characteristic are shown in table 1.2.

Table 1.2 Physical characteristic (Metcalf and Eddy, 1981)

Characteristic	Definition
Total solids	All the matter that remains as residue upon evaporation at 103 to 105 ^{0}C
Settleable solids	Solids that will settle to the bottom of con-shaped container in 60 min period
Total volatile solids	The organic fraction that oxidize and drive off as gas at 550 ^{0}C
Turbidity	Measure of the light transmitting property of water is another test used to indicate the quantity of waste discharge and natural water with respect to colloidal and residual suspended

1.3 Pharmaceutical Wastewater

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 1.3. 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 waters (Carballa et al., 2004; Boyd et al., 2003). 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 (AOPs) are a treatment alternative for a wide variety of recalcitrant micropollutants (Parsons,2004). Some of the most frequently AOPs studied for water treatment applications are UV/O_3 process, $UV\text{-}H_2O_2$, heterogeneous photocatalysis, Fenton and photo-Fenton reaction, sonolysis, supercritical water oxidation, non-thermal plasma, electrolysis, etc. Although several and well differenced mechanisms of degradation appear in each AOP, the hydroxyl radical (·OH) is the powerful oxidizing specie, commonly attributed to oxidative degradation. The hydroxyl radical is a high non-selective reagent and unstable specie with one of the most high redox potential (2.8 E0 V 25ºC) (Blesa et al., 2004). The generation, reaction and deactivation of this radical depend on the particular process applied. The degradation efficiency of organic compound depends strongly on the chemical proprieties of the target compound and the intermediates generated. Several AOPs have shown successful results in the removal of PPCPs, for instance Norflaxin/TiO_2 (Haque et al., 2007), Carbamazapine/$UV\text{-}O_3$ (Doll, 2004), Bisphenol- A/Sonolysis (Torres et al., 2007), Sulfamethoxazole/photo-Fenton (González et al., 2007), etc. The aim of this work is to evaluate the degradation of the pharmaceutical pollutant by the application of some AOPs (UV/Vis-H_2O_2 process, high frequency sonolysis, heterogeneous photocatalysis with TiO_2 and photo-Fenton reaction) and to obtain the mineralization efficiency of each process.

Table 1.3 Chemicals Discharged in Wastewater by the Pharmaceutical Manufacturing Industry

Constituent Name	Quantity Discharged (lbs/yr)	Percent of Total Loading	# of Facilities Reporting Constituents
Methanol	15,388,273	28	82
Ethanol	6,802,384	12	97
Acetone	4,573,766	8.4	55
Isopropanol	4,565,370	8.4	85
Acetic acid	4,328,691	7.9	44
Methylene chloride	3,590,640	6.6	47
Formic acid	2,136,059	3.9	9
Ammonium hydroxide	1,365,741	2.5	32
N1N-Dimethylacetamide	1,046,333	1.9	7
Toluene	783,364	1.4	43

1.4 Occurrence and Fate of Pharmaceuticals in the Environment

Until recently pharmaceutical compounds in the environment have drawn very little attention. Although their in sewage treatment plant effluents was reported (*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, as discussed before (*Ku¨ mmerer, 2001; Debska et al., 2004*). 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 *(Ternes, 1998; Hirsch et al., 1999; Putschew et al., 2000), the Netherlands (Belfroid et al., 1999), Switzerland (Soulet et al., 2002), Canada (Ternes et al., 1999; Miao et al.,2004), Brazil (Ternes et al., 1999), Italy (Castiglioni et al. 2004), Spain (Rodrı´ guez et al., 2003), and the United States (Drewes et al., 2001; 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 ng/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 (*Sacher et al., 2001; Cahill et al., 2004; Clara et al., 2004).* There are several possible sources and routes for the occurrence of pharmaceutical compounds in the aquatic environment (Figure 1). For human pharmaceuticals,non-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 feces and go into a wastewater collection system (*Heberer, 2002; Jones et al., 2005b*). 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 *(Ternes, 1998; Drewes et al., 2001; Miao et al., 2002; Soulet et al., 2002; Jones et al., 2005b).* 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 cleaved by microbial degradation resulting in a release of parent compounds (*Heberer, 2002; Jones et al., 2005b*). 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 reuse.

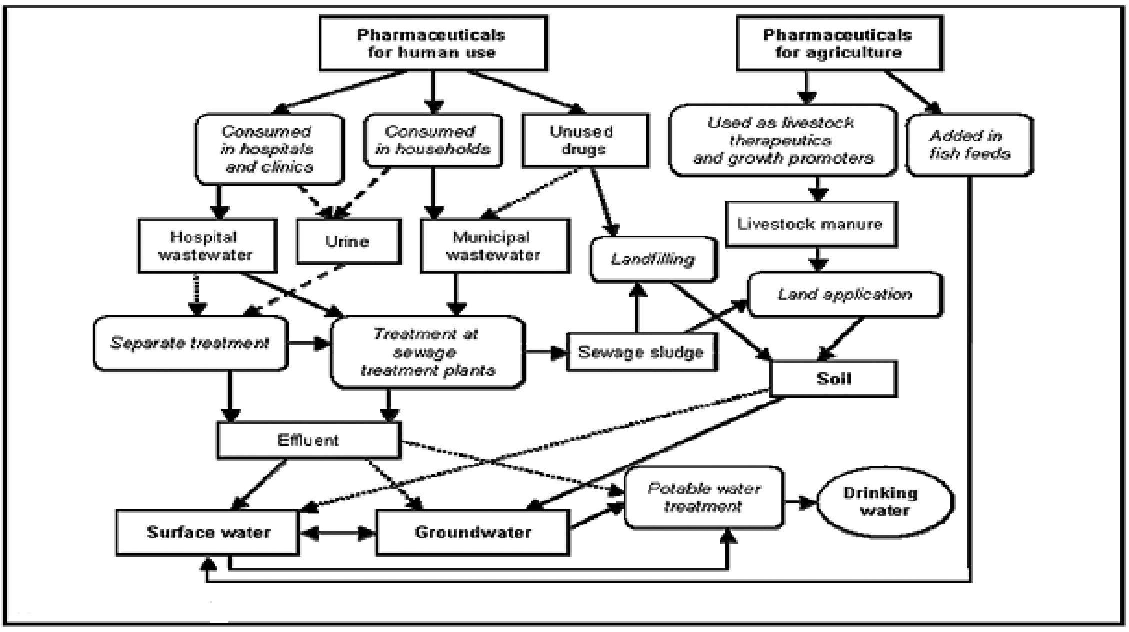


Fig.1.1 Routes of pharmaceutical contamination of the aquatic environment

1.5 Environmental and Public Health Impacts of Pharmaceuticals

After publication of the earlier occurrence data, the risks associated with pharmaceutical contamination of the aquatic environment have become a major issue of concern for environmental scientists and engineers, as well as among the public. Drugs are the chemicals that are designed to give a certain therapeutic (= biological) effect; therefore, certain environmental and public health risks can be anticipated from the exposure to the environmental pharmaceuticals. Besides, there are a few classes of pharmaceuticals that pose unambiguous impacts on the aquatic organisms, including microorganisms, phytoplankton, plants, crustaceans, fish, and insects, as well as on soil microorganisms and possibly humans *(Halling-Sørensen et al., 1998; Sumpter, 1998; Ku¨ mmerer, 2001, 2004*). These pharmaceutical classes include:

-Cytostatic agents, immunosuppressive drugs, and some genotoxic antibiotics because of their evident cytotoxic, carcinogenic, mutagenic, and/or embryotoxic properties;

-Human and veterinary antibiotics because of their pronounced microbial toxicity and the development of antibiotics resistance in environmental bacteria including human pathogens;

-Natural and synthetic hormones because of their high efficiency, low effect thresholds and potential for endocrine disruption;

-Halogenated compounds such as iodinated Xray contrast media because of their resistance toward biodegradation and their mobility and persistence in the environment and the food web;

-Heavy-metal containing drugs and non-therapeutic medical agents because of the toxicity of the metals in certain oxidation states.

In addition, the presence of other types of pharmaceuticals, such as analgesics and anticonvulsants, in drinking water is a potential public health issue. Although the concentrations found in finished water is generally very low, it is apparent that drinking water consumption is the major route of human exposure to the environmental pharmaceuticals (Figure 1). Since the long-term health effects are still largely unknown for the exposure to the trace pharmaceuticals and their metabolites, especially as a mixture of biologically active compounds, the existence of these compounds in drinking water should be avoided on the basis of precautionary principle (*Snyder et al., 2003; Jones et al., 2005a*). Similarly, long-term exposure of aquatic organisms to trace pharmaceuticals in surface water may have some as-yet-known ecological impacts

Pharmaceutical and personal care products (PPCPs) residues have been detected in environmental samples including groundwater, surface water, and municipal wastewater (*Mowery HR et al., 2006*). 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. Azithromycin, a commonly used antibiotic and urobilin, a breakdown product of bilirubin.

In the general context of the environmental problems caused by different kinds of pollutants, four different types of aqueous solutions containing organic compounds as phenol, nitrobenzene, DCDE and water coming from the pharmaceutical industry .

Phenols have been widely used in many industrial processes, as synthesis intermediates or as raw materials in the manufacturing of pesticides, insecticides, wood preservatives, petroleum refining and petrochemicals, pharmaceuticals, paint and dye industries, organic chemicals manufacturing and so forth. Because of the great diversity of their origins, they have a great ubiquity and can be found not only in industrial wastewaters but also in soils and surface and ground waters, as a consequence of their release in industrial effluents or improper waste disposal practices and accidental leakages.

Aromatic nitro compounds are commonly used in the manufacture of pesticides, dyes and explosives, and are often detected in industrial effluents, in ambient freshwater, in ambient environments and in the atmosphere. Moreover, nitro aromatic hydrocarbons are naturally generated, as results of photochemical reactions produced in the atmosphere (in countries like Germany, Japan, Switzerland and USA nitro phenol and dinitrophenol have been detected in air and rain).

Dichlorodiethylether (DCDE) is widely used in the US in the manufacture of pesticides and pharmaceuticals, as a solvent and cleaning fluid, as a constituent of paints and varnishes, and in the purifying of oils and gasoline.

1.6 Wastewater Discharge Standards for Pharmaceutical Industries

As environmental regulations become more stringent, many plants will be required to effluent treatment before discharging their wastewater into the environment. Research and development for the advancement of wastewater treatment are always under process, but existing treatment methods in a chemical and pharmaceutical industry has difficulty to remove the contaminants as per the discharge standards given in Table 1.4.

Table 1.4: National Environmental Quality Standards (NEQS) of Pharmaceutical Effluent

	Parameter	Concentration not to exceed limits in mg/l (except pH)
Compulsory	pH	6.5-8.5
	Oil & Grease	10
	BOD(3 days at 27^0C)	100
	Total Suspended Solids	100
Additional	Mercury	0.01
	Arsenic	0.2
	Chromium(hexavalent)	0.1
	Lead	0.1
	Cyanide	0.1
	Phenolics(C_6H_5OH)	1.0
	Sulfides(as S)	2.0
	Phosphate(as P)	5.0

Note: All values are in parts per million except pH Source: CPCB

1.7 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 effluent of Pharmaceutical industry using heterogeneous photocatalytic treatment. During this project, samples of the untreated effluent and final clarifier effluent was collected and tested in the environmental laboratories. The photocatalytic treatment does not transfer pollutants from one phase to another and leads to complete degradation of organic non biodegradable compounds into simpler end products. The study was undertaken with the following objectives:

- Characterization of effluent
- Photocatalytic treatment of real pharmaceutical effluent
- Effect of variables on degradation efficiency and its optimization

CHAPTER-2

CONVENTIONAL TREATMENT TECHNOLOGY

The treatments processes of different types of effluents to be used must guarantee the elimination of the pollutant in order to reach the strict authorized levels for the discharge of these effluents. The levels of pollutants allowed in discharge waters, are directly related with the type of present pollutant present in the effluent. In general, the elimination of organic pollutants in aqueous solution need one or various basic treatment techniques *(Naresh N. Mahamuni et. al 2006)*, many processes such as membrane separation, wet air oxidation, radiolysis, Fenton oxidation, photo catalytic oxidation, electrochemical oxidation, ozonation, per oxidation and sonication had been used for the degradation of organic compounds to the required low levels. These processes had been used alone or in combination with other processes to achieve the aim. But all these processes have their inherent limitations such as low rates of degradation, or lower mineralization or high costs of operation or severe operating conditions, etc.

Conventional wastewater treatment methods such as Coagulation/Flocculation, adsorption and biological treatment, chlorination, membrane separation etc. do not involve chemical transformations and generally transfer waste component from one phase to another, thus causing secondary loading of environment and waste disposal problem (*Jian-Hui Sun et. al 2006)*. Biological methods are amenable only for biodegradable pollutants as in the case of domestic waste water and industrial effluent in a limited ways.

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Depending upon waste water characteristics, waste water treatment methods should be used.

2.1 Treatment of Industrial Wastewater

At wastewater treatment plants, this flow is treated before it is allowed to be returned to the environment, lakes, or streams. There are no holidays for wastewater treatment, and most plants operate 24 hours per day every day of the week. Wastewater treatment plants operate at a critical point of the water cycle, helping nature defend water from excessive pollution. Most treatment plants have primary treatment (physical removal of floatable and settle able solids) and secondary treatment (the biological removal of dissolved solids). Generally in wastewater treatment the following steps are:

1. Preliminary treatment
2. Primary treatment
3. Secondary treatment
4. Tertiary treatment

2.1.1 Preliminary treatment

The purpose of preliminary treatment is to protect the operation of the wastewater treatment plant. This is achieved by removing from the wastewater any constituents which can clog or damage pumps, or interfere with subsequent treatment processes. Preliminary treatment devices are, therefore, designed to:

1. Remove or to reduce in size the large, entrained, suspended or floating solids. These solids consist of pieces of wood, cloth, paper, plastics, garbage, etc. together with some fecal matter.
2. Remove heavy inorganic solids such as sand and gravel as well as metal or glass. These objects are called grit.
3. Remove excessive amounts of oils or greases.

A number of devices or types of equipment are used to obtain these objectives. **Racks and Bar Screens-** These consist of bars usually spaced three-quarter inches to six inches. Those most commonly used provide clear openings of one to two inches. Although large screens are sometimes set vertically, screens are usually set at an angle of 45 to 60 degrees with the vertical. The incoming wastewater is passed through the bars or screens and periodically the accumulated material is removed. The racks or screens may be cleaned either manually or by means of automatically operated rakes. The solids removed by these units can be disposed of by burial or incineration.

Grit chamber- Wastewater usually contains a relatively large amount of inorganic solids such as sand, cinders and gravel which are collectively called grit. The amount present in a particular wastewater depends primarily on whether the collecting sewer system is of the sanitary or combined type. Grit will damage pumps by abrasion and cause serious operation difficulties in sedimentation tanks and sludge digesters by accumulation around and plugging of outlets and pump suctions. Consequently, it is common practice to remove this material by grit chambers. Grit chambers are usually located ahead of pumps or comminuting devices, and if mechanically cleaned, should be preceded by coarse bar rack screens.

Oils and grease removal- Many oils can be recovered from open water surfaces by skimming devices. However, hydraulic oils and the majority of oils that have degraded to any extent will also have a soluble or emulsified component that will require further treatment to eliminate. Dissolving or emulsifying oil using surfactants or solvents usually exacerbates the problem rather than solving it, producing a very difficult to treat wastewater.

The wastewaters from large-scale industries such as oil refineries, petrochemical plants, chemical plants, and natural gas processing plants commonly contain gross amounts of oil and suspended solids. Those industries use a device known as an API oil-water separator which is designed to separate the oil and suspended solids from their wastewater effluents. The name is derived from the fact that such separators are designed according to standards published by the American Petroleum Institute (API).

The API separator is a gravity separation device designed by using Stokes Law to define the rise velocity of oil droplets based on their density and size. The design is based on the specific gravity difference between the oil and the wastewater because that difference is much smaller than the specific gravity difference between the suspended solids and water. The suspended solids settles to the bottom of the separator as a sediment layer, the oil rises to top of the separator and the cleansed wastewater is the middle layer between the oil layer and the solids.

Typically, the oil layer is skimmed off and subsequently re-processed or disposed of, and the bottom sediment layer is removed by a chain and flight scraper (or similar device) and a sludge pump. The water layer is sent to further treatment consisting usually of a dissolved air flotation (DAF) unit for additional removal of any residual oil and then to some type of biological treatment unit for removal of undesirable dissolved chemical compounds.

2.1.2 Primary treatment

It involves various physical and chemical processes Sedimentation tank (settling tank or clarifier)-Most solids can be removed using simple sedimentation techniques with the solids recovered as slurry or sludge. Very fine solids and solids with densities close to the density of water pose special problems. In such case filtration or ultra-filtration may be required. Alternatively, flocculation may be used using alum salts or the addition of poly-electrolytes

2.1.3 Secondary treatment

It typically utilizes biological treatment processes, in which microorganisms convert nonsettleable solids to settle able solids. Sedimentation typically follows, allowing the settle able solids to settle out. Three options include:

Activated Sludge- The most common option uses microorganisms in the treatment process to break down organic material with aeration and agitation, then allows solids to settle out. Bacteria-containing “activated sludge” is continually recirculated back to the aeration basin to increase the rate of organic decomposition.

Trickling Filters- These are beds of coarse media (often stones or plastic) 3-10 ft. deep. Wastewater is sprayed into the air (aeration), and then allowed to trickle through the media. Microorganisms attached to and growing on the media, break down organic material in the wastewater. Trickling filters drain at the bottom; the wastewater is collected and then undergoes sedimentation.

Lagoons- These are slow, cheap, and relatively inefficient, but can be used for various types of wastewater. They rely on the interaction of sunlight, algae, microorganisms, and oxygen (sometimes aerated).

2.1.4 Tertiary treatment

An increasing number of wastewater facilities also employ tertiary treatment, often using advanced treatment methods. Tertiary treatment may include processes to remove nutrients such as nitrogen and phosphorus, and carbon adsorption to remove chemicals. These processes can be physical, biological, or chemical. Settled solids (sludge) from primary treatment and secondary treatment settling tanks are given further treatment and undergo several options for Sludge Treatment and Disposal.

The removal of contaminant from industrial waste water tertiary method is used. These are Incineration, Air stripping, Adsorption processes, Wet oxidation, electrochemical oxidation, photochemical processes, Biological oxidation, ultrasonic treatment and Chemical oxidation such as UV-based processes as well as H_2O_2 –based processes.

2.2 Treatment of Organics Waste

Synthetic organic materials including solvents, paints, pharmaceuticals, pesticides, coking products and so forth can be very difficult to treat. Treatment methods are often specific to the material being treated. Methods include distillation, adsorption, vitrification, incineration, chemical immobilisation or landfill disposal. Some materials such as some detergents may be capable of biological degradation and in such cases, a modified form of wastewater treatment can be used.

2.3 Treatment of Acids and Alkalis

Acids and alkalis can usually be neutralized under controlled conditions. Neutralization frequently produces a precipitate that will require treatment as a solid residue that may also be toxic. In some cases, gasses may be evolved requiring treatment for the gas stream. Some other forms of treatment are usually required following neutralization.

Waste streams rich in hardness ions as from de-ionisation processes can readily loose the hardness ions in a buildup of precipitated calcium and magnesium salts. This precipitation process can cause severe furring of pipes and can, in extreme cases, cause the blockage of disposal pipes.

2.4 Treatment of Toxic Materials

Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. Many, however, are resistant to treatment or mitigation and may require concentration followed by landfilling or recycling.

CHAPTER-3

ADVANCED OXIDATION PROCESSES

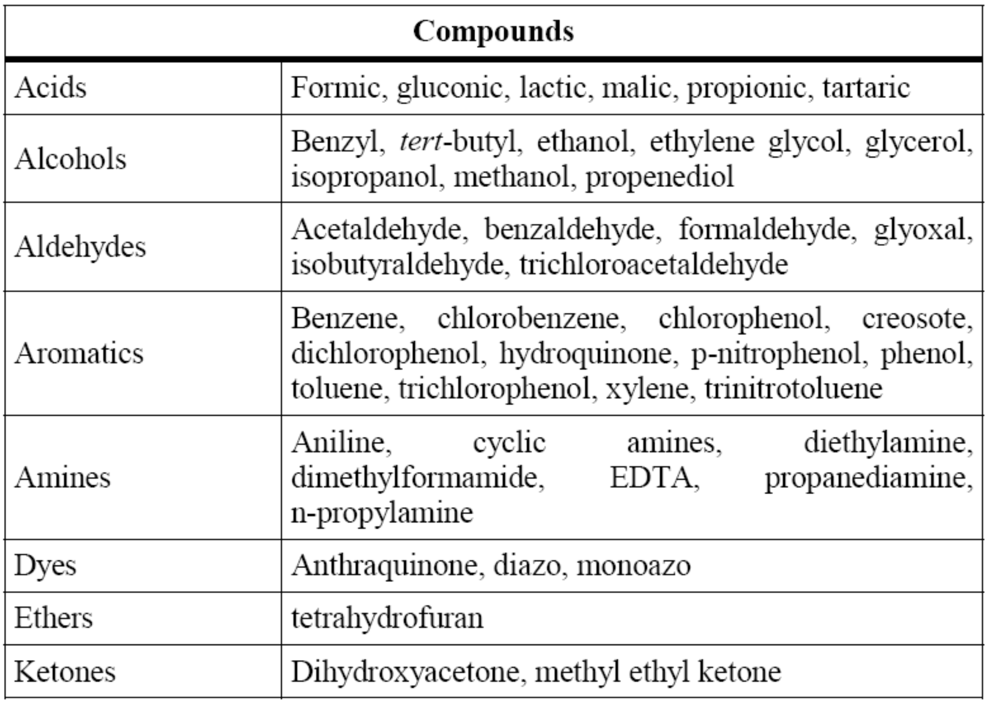
AOPs were defined by Glaze and et al. (1987) as ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive species that attack most of the organic molecules. The kinetics of reaction is generally first order with respect to the concentration of hydroxyl radicals and to the concentration of the species to be oxidized. Rate constants are usually in the range of 10^8-10^{11} L.mol^{-1}.s^{-1} whereas the concentration of hydroxyl radicals lays between 10^{-10} and 10^{-12}mol.L-1, thus a pseudo-first order constant between 1 and 10^{-4}s^{-1}is obtained (*Glaze and Kang, 1989*). As it can be seen hydroxyl radicals are more powerful oxidants than the chemical agents used in traditional chemical processes.

Hydroxyl radicals are also characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment. Several and different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals, as it is shown in Table 3.1. Nevertheless, some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives as chloroform or tetrachloroethane, cannot be attacked by OH* radicals (*Bigda, 1995*). Depending upon the nature of the organic species, two types of initial attacks are possible: the hydroxyl radical can abstract a hydrogen atom to form water, as with alkanes or alcohols, or it can add to the contaminant, as it is the case for olefins or aromatic compounds.

The versatility of AOPs is also enhanced by the fact that they offer different ways of HO* radicals production, thus allowing a better compliance with the specific treatment requirements. It has to be taken into account, though, that a suitable application of AOPs to wastewater treatment makes use of expensive reactants as hydrogen peroxide and/or ozone, and therefore they should not replace, whenever possible, the more economic treatments as the biological degradation.

As hydroxyl radicals are so reactive and unstable, they must be continuously produced by means of photochemical or chemical reactions. The main processes of producing these radicals are described below. It is very difficult to make a classification of the advanced oxidation processes, for the diverse combinations that are presented among them. For this reason, they are presented in the way that has been considered more appropriate.

Table 3.1: Oxidizable compounds by hydroxyl radicals (Bigda, 1995)



Compounds	
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

3.1 UV-Based Processes

As it has been commented previously, the slow kinetics achieved by photochemical reactions can be enhanced by the addition of hydrogen peroxide and/or ozone, metallic salts or semiconductors. The UV/oxidizer system involves direct excitation of the substrate due to the radiation with the subsequent oxidation reaction. Even so, there may be synergism between the oxidizer and the ultraviolet radiation, which causes the global effect to be different from the additive effect.

3.1.1 UV/O_3 process

The UV/O_3 system is an effective method for the oxidation and destruction of organic compounds in water. Basically, aqueous systems saturated with ozone are irradiated with UV light of 253.7 nm. The extinction coefficient of O3 at 253.7 nm is 3300 L.mol-1.cm-1, much higher than that of H_2O_2 (18.6 L.mol-1.cm-1). The decay rate of ozone is about a factor of 1000 higher than that of H2O2 (Guittonneau *et al.*, 1991).

The AOP with UV radiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone leads to two hydroxyl radicals, which do not act as they recombine producing hydrogen peroxide (*Peyton and Glaze, 1988*):

$$H_2O_2 + O_3 \xrightarrow{h\nu} 2\,HO^{\bullet} + O_2$$

$$2\,HO^{\bullet} \rightarrow H_2O_2$$

This system contains three components to produce OH radicals and/or to oxidize the pollutant for subsequent reactions: UV radiation, ozone and hydrogen peroxide. and therefore they should not replace, whenever possible, the more economic treatments as the biological degradation.

As hydroxyl radicals are so reactive and unstable, they must be continuously produced by means of photochemical or chemical reactions. The main processes of producing these radicals are described below. It is very difficult to make a classification of the advanced oxidation processes, for the diverse combinations that are presented among them. For this reason, they are presented in the way that has been considered more appropriate.

3.1.2 UV/O_3 /H_2O_2 process

The addition of H_2O_2 to the UV/O_3 process accelerates decomposition of ozone resulting in increased rate of HO* 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. *Mokrini et al. (1997*) presented the degradation of phenol by means of this process at different pHs, establishing the optimal H2O2 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. With regards to DCDE and textile wastewaters no articles have been found in the literature about the oxidation of these compounds by means of this combined process.

3.1.3 Fe^{3+} / UV-VIS process

Among the AOPs, the iron photo-assisted system stem Fe^{3+} /UV-vis, without addition of other electron acceptor than O_2 from air, has received special attention as a potential wastewater treatment process. The interesting point in such a system, compared to the photo-Fenton process is that no addition of hydrogen peroxide is needed. The excitation of $[Fe(OH)(H2O)5]^{2+}$, the dominant monomeric species of aqueous ferric ion in acidic solution, is known to yield HO* with a quantum yield of 0.075 at 360 nm (*Benkelberg and Warneck, 1995).*

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet}$$

where $Fe(OH)^{2+}$ refers to $[Fe(OH)(H2O)5]^{2+.}$

This electron transfers process has been efficiently used to study the degradation of several organic pollutants in aqueous solution (*Nansheng et al., 1996; Brand et al., 1997*; *Catastini et al., 2001). Mazellier and Bolté (1999, 2001*) used this process for the degradation of 4- and 3-chlorophenol in aqueous solution. The process was found to be an efficient photoinducer of these phenolic compounds.

3.1.4 UV/TiO_2 (Heterogeneous photocatalysis)

Over the last few years the tendency has been to carry out chemical oxidation in the presence of a catalyst that serves as a generator of hydroxyl radicals, and, therefore, the addition of an oxidizer in the medium is not necessary.

Heterogeneous photocatalytic process consists on utilizing the near UV radiation to photo excite a semiconductor catalyst in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radical or free holes, are generated. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of solar spectrum (wavelength shorter than 380 nm) what transforms it into a good option to be used at big scale (*Malato et al., 2002*).

Many catalysts have been tested, although TiO_2 in the anatase form seems to possess the most interesting features, such as high stability, good performance and low cost (*Andreozzi et al., 1999*). It presents the disadvantage of the catalyst separation from solution, as well as the fouling of the catalyst by the organic matter.

Minero et al. (1994) studied the photocatalytic degradation of NB 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)*. Regarding DCDE, no references about the use of photocatalysis heterogeneous has been found. Few studies have been found in the literature regarding the photocalytic oxidation of textile wastewaters (*Balcioglu and Arslan, 1999*).

3.2 H_2O_2 -Based Processes

The most important advanced oxidation treatments based in the use of H_2O_2 are:

- H_2O_2/UV
- H_2O_2 /O_3 process and
- Fenton and photo-Fenton process.

3.2.1 H_2O_2 /UV process

This AOP process is, the H_2O_2/UV system involves the formation of HO· 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:

$$H_2O_2 \xrightarrow{hv} 2OH^*$$

It presents the advantage compared when working with ozone that it provides a cheap and sure source of radicals, eliminating this way the problem of the handling of ozone. The major drawback of this process is that if the solution presents a strong absorbance this can compete with hydrogen peroxide for the radiation, thus cloudy waters or containing compounds absorbing UV radiation can present problems at being treated by this method.

The effectiveness of the UV/H_2O_2 system in the treatment of aromatic compounds such phenol and NB has been widely studied (*e.g. García et al., 1989 and*

Lipczynska- Kochany et al; 1992). However, in the case of DCDE, no reference was found. (*Alaton and Balciogl et al; 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.

3.2.2 H_2O_2 /O_3 process

Addition of hydrogen peroxide to ozone offers another way to accelerate the decomposition of ozone, leading to the formation of OH radicals. Hydrogen peroxide in aqueous solution is partially dissociated in the hydroperoxide anion (HO^{2-}), which reacts with ozone, decomposing this and giving rise to a series of chain reactions with the participation of hydroxyl radicals. In the global reaction two ozone molecules produce two hydroxyl radicals (Glaze and Kang, 1989).

$$H_2O_2 + 2O_3 \longrightarrow 2HO^* + 3O_2$$

As this system does not depend on the UV radiation transmission to activate the ozone or hydrogen peroxide molecules, its greatest advantage is to be able to work with turbid waters without problems. Balcioglu and Arslan (2001) studied the efficiency of ozonation and O_3/H_2O_2 of reactive dyes and textile dye-bath wastewater. They found a considerable improvement in COD and color removal rates at pH=11, which is normally the pH of textile wastewaters.

3.2.3 Fenton and photo-Fenton reaction

The Fenton reaction was discovered by H.J.Fenton in 1894 (Fenton, 1894). Forty years later the Haber-Weiss (1934) mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. Since then, some groups have tried to explain the whole mechanism (Walling, 1975; Sychev and Isak, 1995) that will be treated in details in the next two chapters. The Fenton reaction can be outlined as follows:

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+1)+} + HO^- + HO^*$$

where M is a transition metal as Fe or Cu.

In the absence of light and complexing ligands other than water, the most accepted mechanism of H_2O_2 decomposition in acid homogeneous aqueous solution, involves the formation of hydroxyperoxyl (HO_2^*/O_2^-) and hydroxyl radicals HO^* (*De Laat and Gallard, H., 1999; Gallard and De Laat, 2000).*

The $HO*$ radical mentioned before, once in solution attacks almost every organic compound. The metal regeneration can follow different paths. For Fe2+, the most accepted scheme is described in the following equations (Sychev and Isak, 1995).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{*} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{*} + H^{+} \qquad (2)$$

$$Fe^{2+} + HO^{*} \rightarrow Fe^{2+} + HO^{*} \qquad (3)$$

$$HO^{*} + H_2O_2 \rightarrow HO_2^{*} + H_2O \qquad (4)$$

$$Fe^{3+} + HO_2^{*} \rightarrow Fe^{2+} + H^{+} + O_2 \qquad (5)$$

$$Fe^{3+} + O_2^{*} \rightarrow Fe^{3+} + O_2 \qquad (6)$$

$$Fe^{2+} + HO^{*} \rightarrow Fe^{3+} + HO_2^{-} \qquad (7)$$

Fenton reaction rates are strongly increased by irradiation with UV/visible light (*Ruppert et al., 1993; Sun and Pignatello, 1993*). During the reaction, Fe^{3+} ions are accumulated in the system and after Fe^{2+} ions are consumed, the reaction practically stops. Photochemical regeneration (eq 1.17) of ferrous ions (Fe2+) by photoreduction of ferric ions (Fe^{3+}) is the proposed mechanism (*Faust and Hoigné, 1990*). The new generated ferrous ions reacts with H_2O_2 generating a second $HO*$ radical and ferric ion, and the cycle continues.

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + HO^{*}$$

Fenton and photo-Fenton reaction depend not only on H_2O_2 concentration and iron added, but also on the operating pH value .

Chamarro et al. (2001) used the Fenton process for the degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene. The stoichiometric coefficient for the Fenton reaction was approximately 0.5 mol of organic compound/mol H_2O_2. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water. Regarding DCDE, has been confirmed that DCDE's biodegradability can be enhanced by modified Fenton's reagent (*Kaludjerski, 2001*). Some works about textile waters treatment by means of Fenton and photo-Fenton process have been published. Most of them showed their effectiveness for color removal and COD reduction (*Balanosky et al., 1999; Kang et al., 2000; Perez et al., 2002).*

An improvement of photo assisted Fenton processes is the UV-vis/ferrioxalate/H_2O_2 system, which has been recently demonstrated to be more efficient than photo-Fenton for the abatement of organic pollutants (*Zepp et al., 1992; Safarzadeh-Amiri et al., 1996*).

Recently, two new electrochemical procedures for the detoxification of acidic waste waters, the so-called electro-Fenton and photoelectro-Fenton processes, where H_2O_2 is electrogenerated, have been developed and have shown their good efficiencies for the mineralization of aniline *(Brillas et al., 1998a*), 4-chlorophenol (*Brillas et al., 1998b*) and 2,4-D (*Brillas et al., 2000*).

3.3 Photocatalysis

The word photo catalysis 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.

Hence, photo catalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself

Present Technology-Today, semiconductors are usually selected as photo catalysts, because semiconductors have a narrow gap between the valence and conduction bands. In order for photocatalysis 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.

Among the possible semiconductors, TiO_2, or Titanium Dioxide, ($E_g = 3.2$ eV) is most extensively used because it has many advantages. It is inert and resistant to corrosion, and it requires little post-processing, making it inexpensive. Finally, it can react under mild-operating conditions. However, it currently needs to use ultraviolet light for photocatalysis to occur. In chemistry**,** photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photo generated catalysis the photo catalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl ions; OH^-) able to undergo secondary reactions. Its comprehension has been made possible ever since the discovery of water electrolysis by means of the titanium dioxide. Commercial application of the process is called Advanced Oxidation Processes (AOP). There are several methods of achieving AOP's that can but do not necessarily involve TiO_2 or even the use of UV. Generally the defining factor is the production and use of the hydroxyl ion.

Examples:

- Conversion of water to hydrogen gas by water splitting photo catalysis. An efficient photo catalyst in the UV range is based on a Sodium tantalum oxide $NaTaO_3$ with co catalyst nickel oxide. The surface of the Sodium tantalum oxide crystals is grooved with so called nanosteps that is a result of doping with Lanthanum (3-15 nm range, see nanotechnology). The NiO particles which facilitate hydrogen gas evolution are present on the edges, the oxygen gas evolves from the grooves.
- Use of titanium dioxide in self cleaning coatings. Free radicals generated from TiO_2 oxidize organic matter.

Oxidation of organic contaminants using magnetic particles that are coated with titanium dioxide nanoparticles and agitated using a magnetic field while being exposed to UV light.

The efficiency of chemical transformation in a photo catalytic system is dependent on the band structure of the photo catalytic and the photo activity of the adsorbate molecules.electon – hole recombination on most semiconductor materials is usually very fast, for example, typically less than 10 nanoseconds for TiO_2. Stability of the catalyst, efficiency of the photo catalytic process, selectivity of the products and the wavelength range response are the main factors determining the overall activity of a particular photo catalyst. A number of semiconductor photo catalysts have been explored for the photo catalytic redox reactions. Examples with wide band gap energies include WO_3, TiO_2, ZnO, and Fe_2O_3. Others such as CdS, ZnS, V_2O_5, ZrO_2, SnO_2, CeO_2, Sb_2O_4 and CdSe have also been found to exhibit photo catalytic activity, but only to a very small extent, compared to Titania or ZnO. Among the numerous photo catalysts, degussa P25 TiO_2 has been the most favored for photo catalytic applications, on account of its high catalytic efficiency, good stability over a wide range of pH and reusability without loss in activity. However, ZnO as been found to be an alternative to TiO_2 and has been to proved to be more effective than TiO_2 in many applications. Due to its large band gap, Titania is suitable more for UV- light mediated processes tan solar light –induced reactions. Small band -gap semiconductors, such as CdS, ZnS are capable of functioning as photo catalysts in redox reactions in the visible region of the solar spectrum, but are unstable and often photo degrade with time.

A variety of coupled semiconductors such as, CdS-ZnS, ZnO- Fe_2O_3, ZnO- SnO_2, and Fe_2O_3-TiO_2, perovskite-type oxides, like,$SrTiO_3$,metal ion –doped TiO_2 and ZnO, semiconductor oxides immobilized on inert supports like glass surfaces, fibres, polythene films, and metallic supports, nanocrystalline particles of titania, hybrid photo catalysts containing titania loaded onto activated carbon have found specific use in the photo-oxidative degradation of a large number of inorganic and organic pollutants. Non semi conducting oxides possessing wide band gap, e.g. zeolites, sulphated zirconia, MgO and CaO constitute a new, promising class of photo catalyst, capable of bringing about photo induced processes in the visible region.

The photo catalyst such as titanium dioxide and zinc oxide could be easily separated from the treated effluents by Filtration/Centrifugation and could be reused repeatedly without much loss in their in photo catalytic activity.

3.3.1 History of Photo catalysis

We are surrounded by photochemistry everyday; we see it in the green color of grass and leave every summer day. However, the first mention of photo catalysis was by Plotnikov in the 1930's in his book entitled Allaemeine photochemie. The next major development followed in the 1950's when Markhani and Laidler performed a kinetic study of photo oxidation on the surface of zinc oxide in an aqueous suspension. By the 1970's researchers started to perform surface studies on photo catalysts like Zinc Oxide and Titanium dioxide. Titanium Dioxide may come in the anatase or the rutile form. Degussa P25 Titanium Dioxide contains both the anatase and rutile form. Curiously, this mixture long stood as the standard in photo catalysis with high reactivity. In the 1970's solar energy was being studied due to a need for more available renewable resources and environmental concerns; photochemistry was looked upon for the storage and usage of solar energy. In 1972 Fujishima and Honda had a breakthrough for the photolysis of water with a semiconductor electrode, which could also be a solar powered cell. The next big breakthrough in photochemistry occurred in 1976 when Carey and Oliver developed a method for measuring the variation in quantum efficiency with intensity .The interest in using Titania as a photo catalyst has since been revived in the 1990.

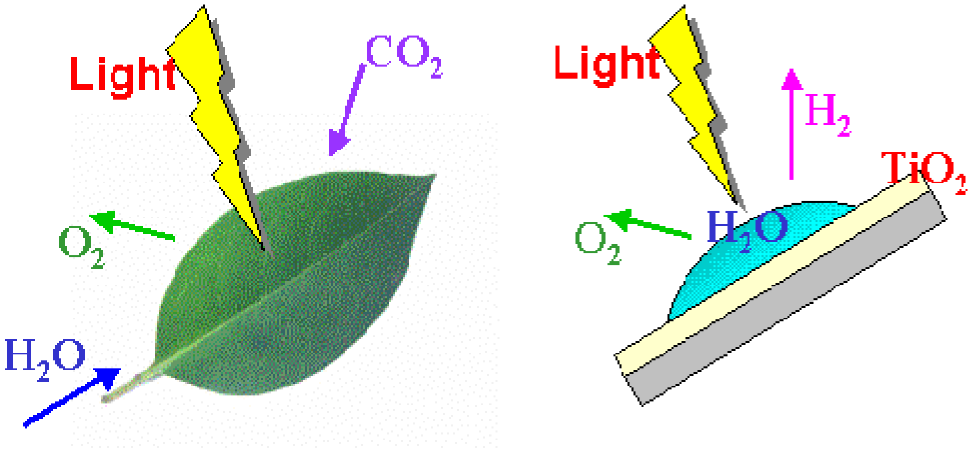
In the 1980's and 1990's there came an increasing concern for environmental preservation and cleanup. As a result some environmental scientists have looked at photochemistry for air, water, and soil cleanup $Ti0_2$ catalyzed photochemistry can accomplish the rnineralization, which is the degradation of organic compounds to H_2O and CO_2 and its inorganic substituants if the organic compound should have any**,** of many different organic compounds.

During the last few years, semiconductor mediated photo catalysis has been reported as a promising route to destroy toxic and hazardous organic substances in industrial wastewater and drinking water. In most cases, a complete oxidative destruction of pollutants has been observed and the end products include CO_2, H_2O and inorganic ions. The harvest of sunlight for photo catalysis has been a tremendous boon to the process, on account of the economic feasibility, ease of large scale operation and process efficiency.

3.3.2 Principle of photo catalysis

It is a process in which the initial absorption of photons by a semiconductor, leads to the formation of electrons and holes. The band structure of the electronic energy levels of the semiconductor consists of the highest occupied band, called the valence band and the lowest unoccupied band called the conduction band separated by band gap energy Ebg. The band gap energy falls in the UV-- Visible region of the electromagnetic spectrum. Hence activation of the semiconductor surface (SC) with UV or Visible radiation results in the promotion of the valence band electron to the conduction band, generating electron(e^-) / hole (h^+) pairs.

$$\text{SC} \text{ ------------}\rightarrow e^- + h^+$$



·Light is absorbed by chlorophyll.

·Light is absorbed by titanium dioxide.

The decomposition reaction of water is slow; thus organic materials, if any, are decomposed preferentially.

Fig3.1 The photosynthetic reaction in plants is basically similar to the photocatalytic reaction in titanium oxide.

In aerated aqueous suspensions of the semiconductor in contact with organic substances, the photogenarated e^-/h^+ pairs initiate a series of redox reactions via a number of mechanisms which include:

1) Oxidation of adsorbed water molecules and hydroxyl ions by photo generated holes to give hydroxyl radicals

$h^+ + OH^-$ ------------------ $OH^{\bullet}$

$h^+ + H_2O$ ---------------- $OH^{\bullet} + H^+$

2) Reduction of dissolved oxygen by the photo generated electrons to produce super oxide anions radicals, which in turn, can lead to generation of H_2O_2 through a series of redox reactions

$O_2 + e^-$ -------------------- O_2^-

$O_2^- + H^+$ ------------------- $HO_2^{\bullet}$

$HO_2^{\bullet} + HO_2^{\bullet}$ ---------------$H_2O_2 + O2$

$^{\bullet}O_2^- + HO_2^{\bullet}$ ----------------- $HO_2^- + O_2$

HO2- + H^+ ------------------ H_2O_2

3) The photo generated hydrogen peroxide undergoes further decomposition to yield hydroxyl radicals

$H_2O_2 + O_2^{\cdot -}$ -------------- $>OH^{\cdot} + OH^{\cdot -} + O_2$

$H_2O_2 + e^-$ --------------- $>OH^{\cdot} + OH^-$

4) Direct participation of the holes and electrons in oxidation / reduction reactions

5) Formation of singlet oxygen, which can participate in oxidation reaction.

The primary oxidants, viz., hydroxyl radicals, super oxide anion radicals and H_2O_2 are strong, non selective oxidants, capable of initiating a series of oxidative degration reaction of adsorbed organic molecules. Oxidation of organic compounds proceeds through a number of free radical reactions, producing a large number of intermediates, which in turn, undergo oxidative cleavage, ultimately resulting in the formation of carbon dioxide, water and inorganic ions.

3.3.3 TiO_2 as a photocatalyst

It is known that photo catalysts can be either homogeneous or heterogeneous. In a system where a homogeneous photo catalyst is used, the photo catalytic reaction takes place in a homogeneous liquid phase. Examples of such photo catalysts include dye, soluble metal catalysts like copper complexes, tin chloride, palladium chloride, Fenton reagent and hydrogen peroxide.

On the other hand, if a heterogeneous photo catalyst is used the photo catalyst and reactant are present in different phases and the photo catalytic reaction occurs at their interface. Examples of heterogeneous photo catalysts include poiyoxometallates such as $Cs_3PW_{12}0_{40}$**,** TiO_2**,** in the colloidal and powdered form or dyes supported on glass, sand and other materials. Solid TiO_2 absorbs light in the near UV (-350 nm) causing an electron from the valence band to be excited across the band gap of +3.0 eV up to the conduction band containing free electrons.

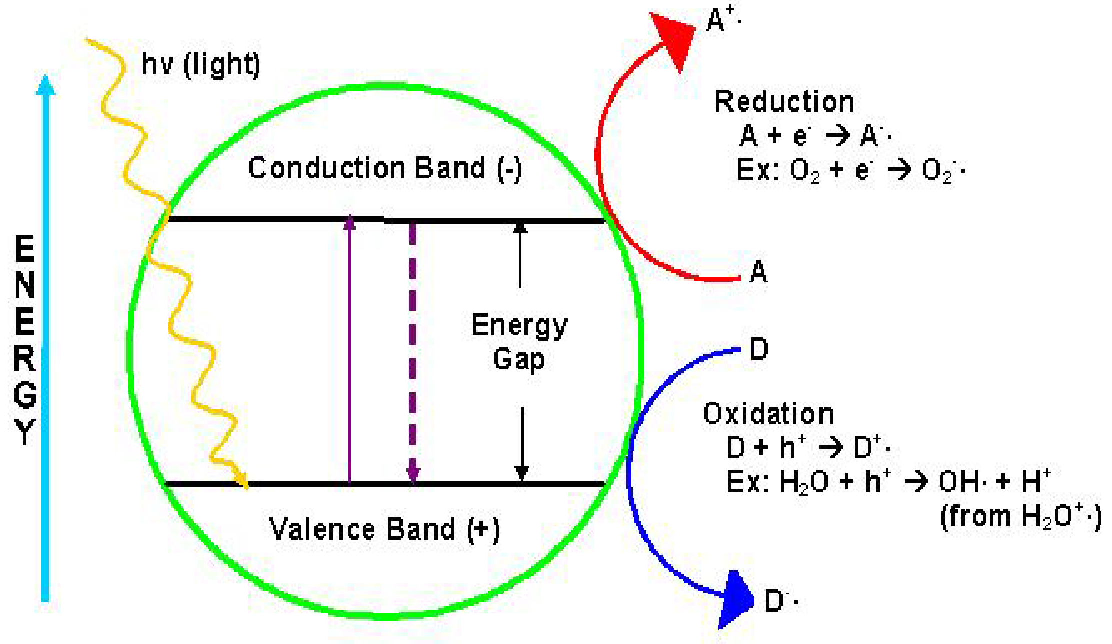


Fig. 3.2 Irradiated TiO_2 particle

It has the ability to produce conductivity similar to that of metals. The carriers may be trapped at or near the $Ti0_2$ particle surface; thus, enabling electron transfer reactions across the interface with a large variety of organic molecules absorbed on the $Ti0_2$ surface from the solution. The potential of the trapped hole carrier is +3.2 V and the electron has a potential of on the hydrogen scale. This makes the hole a powerful oxidizing agent and the electron a good reducing agent. The hole can generate a hydroxyl radical at the surface or a one electron oxidation of a wide range of adsorbed organic molecules can be initiated.

The electron is captured by O_2 to generate the reactive super oxide ion. For the above reasons the illuminated TiO_2 surface is an extremely attractive catalyst for the initiation of the oxidation of a wide range of organic compounds. In most cases the oxidation can proceed to mineralization where the final products are CO_2, H_20 and inorganic ions of other elements that may be present in the organic molecule. As stated earlier the difficulty of handling the material due to the fine particulate nature of TiO_2 along with a relatively high electrical energy cost because the quantum yield is a bit too low, has limited the commercialization and widespread use of this technology.

3.4 Photo Catalysis Oxidation of Water Borne Organic Pollutants

Advanced oxidation processes are chemical treatment given to such type of pollutants, which are not be treated by conventional treatment methods such as coagulation/flocculation, membrane separation (ultrafilteration, reverse osmosis) activated carbon adsorption and biological treatment. Advanced oxidation processes oxidize or mineralize the pollutants into their simpler forms, which are easily biodegradable and so it is facilitating their treatments in conventional processes, which are having an advantage of being cheaper than any other process. AOP’s can be homogeneous and heterogeneous in nature. Homogenous processes include simply the use of some chemicals called homogenous advanced oxidation process. Heterogeneous processes employed some catalyst for the increasing rate of degradation process, called heterogeneous advanced oxidation processes or catalytic oxidation processes. Theses processes are employed in the presence of UV, visible or solar light, for deriving the energy for oxidation of pollutants. So combination of theses process is called photo catalytic processes. These processes may be classified as UV mediated photo catalytic process Visible light induced photo catalytic process and sonophoto catalytic process.

3.5 Application of Advanced Oxidation Processes (AOPs)

Wastewater generated from different industries contains different type of organic compounds which are nonbiodegradable as well as toxic in nature. Treatment of these compounds is very difficult by conventional methods but Advanced oxidation processes could be a good alternative to treat and remove these organic compounds. AOP,s have advantage , they are environmentally friendly methods capable of destroying the organics without the production of harmful by-products and disposal problems. AOP’s are expensive due to high initial and operating cost; however, these are following applications:

1) A common application for TiO_2 photo catalysis is the mineralization of trichlorotmehtane ($CHCl_3$). Trichloromethane is suspected carcinogenic chloroform produced from dissolved organic matter during conventional water chlorination procedures. This purification process is shown to be very effective in an experiment performed by David F. Ollis, a chemical engineer at North Carolina University. According to his results published in Environmental Science and Technology, "The simultaneous presence of illumination and TiO_2 produced the chloride ion and caused

the disappearance of chloroform". The basic general equation for chloroform breakdown is given below:

$H_2O + CHCl_3 + (1/2)\ O_2 => CO_2 + 3HCl$

The oxygen needed for the experiment is aerated throughout the contaminated water. The statement given states that a chloride ion is produced. it shows that the ions combine with hydrogen to form a more desirable compound HCl .

2) Photo catalytic method is effective in destroying benzene, chlorobenzene, chlorophenol, dichloroethene, benzidine, and phenol. Destruction percentages of the test compounds measure using UV to greater than 89%. Destruction of other contaminants can also be achieved by this method.

3.6 Light Sources

TiO_2 absorbs radiation below the visible range of light spectrum. Hence, photoactivation of TiO_2 requires radiation with light of wavelength less than or equal to 384 nm, with an absorbance maximum at approximately 340 nm. The vast majority of studies quoted in the literature have been carried out between the wavelengths 320- 380 nm. The light that gives rise to the required radiation field can be produced by artificial lamps or by solar irradiation. In a photocatalytic reactor, UV-A (320-380 nm) radiation is provided by fluorescent low-pressure mercury lamps emitting low-intensity UV-A radiation. Medium pressure mercury lamps have also been used, which emit high intensity UV light in the short, medium and long UV spectrums. However, short (UV-C; 200-280 nm) and medium (UV-B; 280-320 nm) UV radiation emitted by the mercury is usually cut off by the photoreactor material, unless it is made of quartz. Some studies have also reported increased efficiency with UV-C radiation than UV-A for the degradation of certain organic materials. Direct photolysis and the higher probability of trapping of electron-hole pairs with shorter wavelength excitation were thought to be the possible reasons for such an effect. It is estimated that only 5% of the incident solar irradiation is of use for the TiO_2 band gap photocatalytic reaction. This significantly limits its practical application. Therefore, modification of TiO_2 photocatalysts to enhance light absorption and photocatalytic activity under visible light irradiation is the subject of recent research

CHAPTER-4

LITERATURE REVIEW

Waste water generated from different industries is posing a great threat not only to mankind but also to the landmass fertility as well as natural flora and fauna. In order to meet the stringent international standards, treatment of industrial wastewater is mandatory. Heterogeneous photo catalysis is a process of great potential for pollutant abatement and waste treatment. In order to improve the overall performance of the photo process, heterogeneous photo catalysis is being combined with physical or chemical operations, which affect the chemical kinetics and/or the overall efficiency. This review addresses the various possibilities to couple heterogeneous photo catalysis with other technologies to photo degrade organic and inorganic pollutants dissolved in actual or synthetic aqueous effluents (Vincenzo Augugliaro et al., 2006). A literature survey was carried out to know the latest advancements in the field of heterogeneous photocatalysis.as well as ultrasonic treatment of waste water. This review basically aims at degradation of the pharmaceutical effluent

4.1 Photocatalytic Degradation

The UV-induced photocatalytic degradation of two azo dyes, Methyl Red and Methyl Orange, has been carried out in aqueous media in the presence of oleic acid (OLEA)- and tri-n-octylphosphine oxide (TOPO)-capped anatase TiO_2 nanocrystal powders (mean particle size: 6 nm). Significantly, although all titania catalysts were effective in removing both parent dyes and their related derivatives, the degradation rate by the OLEA-capped TiO_2 nanocrystals was double as that obtained with both its TOPO-capped analogous and TiO_2 P25 Degussa (*R. Comparelli et al., 2005*). Electrochemical-assisted photo degradation of methyl orange has been investigated using TiO_2 thin films. The light sources chosen ranged from ultraviolet to visible light. The effect of agitation of the solution at different speeds has also been studied (*Zulkarnain Zainal et al., 2005*). The photocatalytic activities of the coupled ZnO/SnO_2 photocatalysts, evaluated using the photo degradation of methyl orange as a probe reaction, were also found to be related to the calcinations temperatures and the Sn contents. The photo-stability of the ZnO/SnO_2 photo catalyst was also studied (*Cun Wang et al., 2004*).

Yingxu Chen et al. (2005) investigated the role of these primary oxidants in the photodegradation of an azo dye, Acid Orange 7 (AO7) in UV-illuminated TiO_2 suspension. Little influence of methanol or isopropanol on the degradation was found. Due to the reciprocity of loading TiO_2 and activated carbon, the TiO_2/AC prepared showed high photo activity for the photo oxidation of methyl orange. it was observed that TiO_2/AC has higher decomposition efficiency than pure TiO_2 particles, as well as a mixture of TiO_2 powder with activated carbon (*Youji Li et al., 2005*). The Ethyl Violet (EV) can be degraded efficiently in aqueous TiO_2 dispersions by visible light irradiation. The UV–vis spectra changes during the photodegradation of EV in the aqueous TiO_2 dispersions under visible light irradiation. After irradiation for 68 h, ca. 99% of EV was degraded. During visible irradiation, the characteristic absorption band of the dye decreased rapidly and shifted to lower wavelength but no new absorption bands appeared even in the ultraviolet range ($\lambda > 200$ nm),(*C.C. Chena et.al., 2005*).

The photocatalytic organic content reduction of synthetic municipal wastewater has been studied at pilot plant scale. The solar photocatalytic has been implemented in paper and pulp mill for water detoxification, as pulp effluent contains polyphenolic polymer lignin-non-biodegradable substances. The photocatalytic degradation of dimethoate, an organophosporous pesticide has been investigated (*S.K.Dubey et. al., 2006*).

Bekkouche et al. (2004) studied the adsorption of the micro pollutant on the photocatalyst, mainly the titanium oxide anatase form, is a determining stage in the process of photo degradation. An experimental study carries out the adsorption of phenol, chosen as the model pollutant, on a photocatalyst, titanium oxide anatase (Degussa P25). The aggregation effect of TiO_2 in aqueous solution had an optimal concentration of the catalyst for a concentration of phenol. The adsorption was optimal for a pH between 5 and 6 in the neighborhood of the isoelectric point of TiO_2.*Damien Gumy, 2006* has been investigated the factors influencing photocatalytic drinking water detoxification and disinfection by suspended and fixed TiO_2.

4.2 Photocatalytic Treatment of Industrial Waste Water

A. Alinsafi et. al.,2007 have applied photo catalysis with TiO_2 particles immobilised either on a glass slide or on a non-woven glass fiber fabric has been applied to pure reactive dyes' (azoïc and metal phthalocyanines) solutions as well as textile wastewater containing the same dyes under UV and solar irradiation. Decolourization of textile wastewater was in the range 21–74% under solar irradiation, with COD removal rate between 0.2 and 0.9 g COD/h/m^2.. Performance prediction is therefore difficult but the results are encouraging for textile wastewater remediation. No pH adjustment is necessary and wastewater at high pH can be treated directly after suspended solids removal.

Different parameters were investigated to evaluate their effect on the process removal efficiency of reactive dye from simulated spent reactive dye bath, by solar / TiO_2 / H_2O_2, including H_2O_2 concentration, TiO_2 loading and pH. As a result 99% of reactive dye can be removed at a TiO_2 loading of 400mg/l, H_2O_2 concentration of 150 mg/l and of pH: 5.2. The effect of photocatalytic deactivation of TiO_2 on reactive dye removal was studied for ten number of cycles, and found that the extent of deactivation was high for each consecutive repeated use (*S. S.Reddy et.al, 2005*)

Pekakis PA et.al., 2006 investigated the oxidative degradation of an actual textile dye house wastewater by means of photo catalysis. The UV-A-induced photocatalytic oxidation over TiO_2 suspensions was capable of decolorizing the effluent completely, as well as reducing chemical oxygen demand (COD) sufficiently (COD reduction generally varied between about 40% and 90% depending on the operating conditions) after 4 h of treatment. Two crystalline forms of TiO_2, viz. anatase and rutile, were tested for their photocatalytic activity and anatase was found to be more active than rutile. To assess catalyst activity on repeated use, experiments were performed where the catalyst was recovered and reused. Finally, the luminescent marine bacteria Vibrio fischeri was used to assess the acute ecotoxicity of samples prior to and after the photocatalytic treatment.

Joshi P et. al., 2001 studied the photocatalytic degradation of two simulated textile dye bath wastewaters. Dye bath wastewaters were subjected to photodegradation in a batch annular immersion well photo reactor equipped with a 400W Medium Pressure Mercury Lamp (MPML). The UV illuminated TiO_2 containing aqueous suspensions found to remove color as well as chemical oxygen demand (COD). The photocatalytic activity was monitored by measuring the rates of decolorization and COD removal as a function of concentration of the dye and treatment time. The first order rate constant (k(app)) for decolorization was 3-9 times higher than the k(app) for COD removal.

Heterogeneous photocatalytic oxidation of contaminants present in wastewater produced by a textile industry was carried out. The samples were withdrawn from the plant before and after a traditional biological treatment. The effluents were named A and A' (before the biological treatment), B and B' (after the biological treatment). Polycrystalline TiO_2 (Degussa P25) was used as the catalyst in a batch photoreactor with immersed lamp. An almost complete decolorization was observed after about 0.5 divided by 1 hour for both kinds of effluents, but the decrease of the total organic carbon (TOC) concentration occurred more slowly. The influence of some chemical oxidants, i.e. ozone, hydrogen peroxide and peroxydisulfate on the photo-oxidation rate was also investigated. After addition of H_2O_2 or S_2O_8 (2-) TOC decreased more quickly only for B and B'. The runs performed by using O_3 as bubbling gas showed a mineralization rate higher than that observed in the presence of O_2 (*Augugliaro V et. al., 2002*).

Hu. C et. al., 1999 have been investigated the photodegradation one industrial wool textile wastewater, using TiO_2 suspensions irradiated with a medium pressure mercury lamp. The color removal dyeing wastewater reached to above 90% within 20-30 min. of photocatalytic treatment. Biochemical oxygen demand (BOD) was found to increase, while chemical oxygen demand (COD), total organic carbon (TOC) decreased, so that the ratio of BOD_5/COD of the wastewater increased from original zero up to 0.75. The result implies that photo catalytic oxidation enhanced the biodegradability of the dye-containing wastewater and therefore relationship between decolorization and biodegradability exists.

Heterogeneous photocatalysis may be considered a viable alternative for the removal of refractory organics due to several important advantages such as: complete mineralization or formation of more readily biodegradable intermediates when complex organic compounds are treated, no need of auxiliary chemicals, no residual formation, easily operation and maintenance of the equipment. This paper presents a literature survey of the research conducted in the field of heterogeneous photocatalysis, providing information on the possibilities and efficiencies encountered in the application of this process for industrial wastewater treatment for the removal of different types of refractory organic compounds (*Anca F. C. et. al., 2002*).

Photo degradation of a real textile dyeing wastewater taken from Hilla textile factory in Babylon Governorate, Iraq have been investigated. Photocatalytic degradation was carried out over suspensions of titanium dioxide or zinc oxide under ultraviolet irradiation. Photodegradation percentage was followed spectrophometrically by the measurements of absorbance at max equal to 380 nm. The rate of photo degradation increased linearly with time of irradiation when titanium dioxide or zinc oxide was used. A maximum color removal of 96% was achieved after irradiation time of 2.5 hours when titanium dioxide used at 303K and 82% color reduction was observed when zinc oxide used for the same period and at the same temperature. The effect of temperature on the efficiency of photo degradation of dyestuff was also studied. The activation energy of photo degradation was calculated and found to be equal to 21 ± 1 kJ mol-1 on titanium dioxide and 24 ± 1 kJ mol-1 on zinc oxide (*Abbas J. A. et. al., 2008*).

The oxidative degradation of an actual textile dye house wastewater was investigated by means of photocatalysis in the presence of TiO_2. The UV-A-induced photocatalytic oxidation over TiO_2 suspensions was capable of decolorizing the effluent completely, as well as reducing chemical oxygen demand (COD) sufficiently (COD reduction generally varied between about 40% and 90% depending on the operating conditions) after 4 h of treatment. Two crystalline forms of TiO_2, viz. anatase and rutile, were tested for their photocatalytic activity and anatase was found to be more active than rutile. The extent of photocatalytic degradation was found to increase with increasing TiO_2 concentration up to 0.5 g/L TiO_2, above which degradation remained practically constant, reaching a plateau. Furthermore, textile effluent degradation was enhanced at acidic conditions (i.e. pH ¼ 3) and in the presence of hydrogen peroxide. To assess catalyst activity on repeated use, experiments were performed where the catalyst was recovered and reused; after three successive uses, TiO_2 had sufficiently retained its photo catalytic activity. Finally, the luminescent marine bacteria Vibrio fischeri was used to assess the acute ecotoxicity of samples prior to and after the photocatalytic treatment and it was found that ecotoxicity was fully eliminated following photocatalytic oxidation (*Pantelis A. Pekakis et.al., 2006*).

Several systems are used in photocatalytic degradation; two of them are experimented in the treatment of textile dyes and washing out reagents. The Thin Fixed Film Bed Reactor (TFFBR) and Aerated Cascade photocatalytic reactor ACP models developed to investigate photocatalytic degradation of organic compounds. For the first one the catalyst is fixed while, for the second one the catalyst is hanging in the solutions. The efficiency of the two systems are tested for the solar catalytic treatment of commercial dyes and washing out reagents. The degradation of the black, red, blue and golden dyes shows that the black had the highest TOC degradation than others. Moreover the ACP system was more efficient than TFFBR. The treatment of the washing out reagents in suspended solutions and TFFBR reactor gives a high TOC degradation with the last system comparing to the first one (*Ghozzi K. et.al.,2002*).

4.3 Photocatalytic Degradation Of Pharmaceutical Effluent

F.Mendez-Arriaga et al.(2007) pharmaceutical and personal care products (PPCPs) have been found to be recalcitrant pollutants in water in several countries. Moreover, sewage treatment plants are not able to get the total degradation of this kind of recalcitrant compounds. Due the specific proprieties and original function of the pharmaceutical products, its presence in water represents an important risk against environmental aquatic systems. Advanced oxidation processes (AOPs) have been successfully applied for the removal of several recalcitrant pollutants. In this study, the degradation of the pharmaceutical pollutant ibuprofen in water by UV/Vis-H_2O_2 process, sonolysis, photocatalysis and photo-Fenton have been carried out. Results indicate that the half-lives are 1.2, 7, 12 and 18.5 min for photo- Fenton (100 µM Fe(II) and 2.2µM/min H_2O_2), UV/Vis-H_2O_2 (6.9 µEins/s), sonolysis (300 kHz, 80W) and photocatalysis (1 g/L TiO2) respectively. The mineralization achieved can be described in the order: Sonolysis< UV/Vis-H_2O_2<photo-Fenton≅TiO_2 reaching values between 20 and 80%. For the case of heterogeneous photocatalysis the main by-products generated are the hydroxyl-metabolites. Depending on the oxidation state of the applied process the biodegradability of the treated solution is improved for an optional post-biological application.

Isil Akmehmet Balcioglu et al. (2004) treatment of synthetically prepared antibiotic formulation wastewater with O_3, O_3/H_2O_2*;* and O_3/UV processes was examined. The efficiencies of the treatment processes were compared by means of COD, absorbance removals, and biodegradability enhancement. The efficiencies of O_3/pH = 7, O_3/ pH 12, and O_3/H_2O_2(50 mM) processes were almost identical in terms of COD and UV254 removals. The BOD_5/COD ratio of formulation wastewater increased from 0.02 to 0.38 and 0.5 at the end of 1 hr of ozone treatment at pH = 7 and pH = 12, respectively.

For the formulation wastewater subjected to O_3/UV process at pH = 7, parallel to the UV254 removal efficiency, a 20% increase was obtained in the Oxygen Uptake Rate (OUR) value compared to that of mere ozonation.

Jennifer L.Packer et al. (2003) aqueous photochemistry of four pharmaceutical compounds detected in surface waters (naproxen,diclofenac, ibuprofen, and clofibric acid) was investigating in purified (Milli-Q) water and in Mississippi River water (MRW). Both direct photolysis and hydroxyl radical-mediated indirect photolysis (using a combination of probe and quencher experiments) were studied. Singlet oxygenation was also investigated for naproxen. econd-order rate constants for reaction with hydroxyl radical were determined using Fenton's reagent. Naproxen was rapidly transformed via direct photolysis in sunlight in both Milli-Q and MRW. The radical quencher isopropyl alcohol (IPA), had a similar effect in both systems, and this effect was interpreted as a reaction of a carboxyl radical intermediate of naproxen. Diclofenac was found to undergo rapid direct photolysis under sunlight, confirming the results of prior studies. Addition of led to more rapid transformation, possibly due to formation of other radical species or photoreduction with IPA serving as the H-source. When irradiated under natural sunlight, slow direct photolysis of clofibric acid is observed in Milli-Q water, and a combination of direct photolysis and radical mediated indirect processes appear responsible for clofibric acid photolysis in MRW. The dominant photochemical loss process for ibuprofen irradiated with a medium pressure Hg-vapour lamp was identified as reaction with photo-generated radicals. These results suggest that photolytic processes are important removal mechanisms for pharmaceutical compounds discharged into sunlit surface waters.

CHAPTER-5

MATERIAL AND METHODS

Described in this chapter are the materials and methods used during this research, including the chemicals, glassware instrument like the UV photo reactor, pH meter and analysis by UV-Vis Spectrophotometer, COD digester, Electrical conductivity (EC) measurement, and procedures used to treat the effluent solutions with the UV/TiO_2 catalysis and UV/TiO_2/$Ca(OCl)_2$. The compilation of the varying pH of solution, TiO_2 dosages and the varying UV contact times for the pharmaceutical effluent with varying concentrations .

5.1 Wastewater

Wastewater was collected from the homogenous tank of effluent treatment plant (ETP,s) of Chemical and Pharmaceutical industry . Wastewater sample was highly polluted as the wastewater characteristics showing in table 6.1.

5.1.1 Reagents and Chemicals Used

The photocatalyst TiO_2 (P25) was procured from Degussa Company. Calcium hypochlorite was used as an oxidant. Pharmaceutical effluent was characterized for pH, EC, Turbidity, BOD, COD, TDS, TSS, Color etc. For the determination of BOD, phosphate buffer, Calcium chloride, Magnesium sulphate, Ferric chloride, Magneous sulphate, Potassium iodide, Sulphuric acid, Sodium thiosulphate and Strach as an indicator were used. 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 all the experiments single distilled water were used. Different normality of (0.1, 1M) HCl and NaOH were used for adjustment of pH of wastewater. Calcium hypochlorite is a chemical compound with formula $Ca(ClO)_2$. It is widely used for water treatment and as a bleaching agent (bleaching powder). This chemical is considered to be relatively stable and has greater available chlorine than sodium hypochlorite

5.1.2 Preparation of Oxidant Used

Calcium hypochlorite $Ca(ClO)_2$ solution 0.001M. Dissolve 0.143gm of $Ca(ClO)_2$ dried in distilled water and make total volume one litre

5.2 Instrument used

5.2.1 pH meter

pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of NaOH and HCl. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

5.2.2 Electrical conductivity meter

EC of the samples was determined by using a deluxe conductivity meter model 601 E (Microsil, India). The EC in (mS/cm) of wastewater sample was estimated and before estimation EC meter was calibrated.

5.2.3 Turbidity meter

Turbidity of the samples was measured by Radio Turbidometer, Hatch turbidity was measured as per standards method No. B 2130, page No 2-13, from STANDARD METHODS for the examination of water and wastewater 1989 (17th edition).

5.2.4 Magnetic Stirrer

Magnetic stirrer was used during experimentation to solve the problem of mixing and titanium dioxide remains in suspension.

5.2.5 Air sparger

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

5.2.6 Photo reactor

Photo catalytic treatment of effluent were performed in batch experiments. For photocatalytic treatment UV reactor was used which was rectangular having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of iron. Roof of the reactor was made up of wooden; seven UV tubes (36 Watt each) were attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Four magnetic stirrers were fitted in the reactor to carry out the photo catalytic reaction in slurry mode. Two different view of photoreactor are shown in Fig. - 5.2.1 a and 5.2.1 b.

Fig- 5.1 Outer view of photo reactor

Fig-5.2 Photo reactor at lab level during photocatalytic treatment

5.2.7 Filtration

After photocatalytic treatment by photo reactor effluent sample were filtered through syringe filters having milipore filters of 0.45 um pore size.

5.2.8 COD Digester

COD digester (Hatch) was used for the digestion of samples in the process of COD determination.

5.2.9 Radiometer

Intensity of UV and solar light was measured with Eppley radiometer.

5.2.10 Spectrophotometer

The spectrum was taken with UV-vis. Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer).

5.2.11 Reaction Vessels

Photochemical degradation was carried out in specially designed double walled reaction vessels in the UV chamber/reactor. Glass bowls were used for the photocatalytic reactions having a capacity of 1 L.

The experiments were conducted in batch mode. Constant stirring of the solution was ensured using magnetic stirrers. Reaction vessel with magnetic stirrer is shown in Fig.5.2.11

Fig: 5.3 Reaction vessel with magnetic stirrer during Photocatalytic treatment.

5.3 Methods and Analysis

5.3.1 Collection and storage of wastewater sample

Sample was collected from homogenous tank of effluent treatment plant of pharmaceutcal industry. Sampling vessel was cleaned and rinsed carefully with distilled water and then washed with sample during sample collection. Then effluent was stored in cold store at 4°C within 3 to 4 hrs of collection.

Wastewater sample was analyzed for the COD, BOD, TDS, TSS, Turbidity, pH, EC, etc. The entire experimental test was repeated to get reproducibility of results. Parameters were analyzed by methods given in standard methods for the examination of water and wastewater 1989 (17th edition). Reagents used for the present investigation were of AR Grade and single distilled water was used throughout the study.

5.3.2 pH Estimation

The pH is a logarithmic scale generally used to express the acidic, alkaline or neutral nature of a solution. In fact, it presents the hydrogen ion concentration or, more precisely, the H^+ ion activity in a given solution. The pH value is the best indication of the presence of acid or alkali in the water sample. Due to hydrolysis of dissolved salts, the pH value can decrease or increase beyond neutral value, i.e. 7.0, showing the presence of salts of strong base and weak acid, e.g. Na_2CO_3 increases pH value; salts of weak base and strong acid, e.g. $CaCl_2$ decrease pH level. Thus, a fundamental relationship exists among pH, acidity and alkalinity.

Significance

The pH is an essential factor to be estimated factor to be estimated in each and every phase of water and wastewater treatment. In water the processes involved in the treatment of potable water, such as chemical coagulation, disinfection, softening and corrosion control are pH dependent. In case of wastewater the biological treatment involves decomposition of organic matter available in wastewater by different species of aerobic bacteria. The growth and activity of these depend on the pH level in wastewater. Generation and emission of malodorous gases are also controlled by pH variations. In chemical treatment of wastewater, the coagulation of wastewater, dewatering of sludge and oxidation of certain substances such as cyanide are also pH dependent processes.Hence, accurate measurement and monitoring of this factor in optimum range is of great significance in water and wastewater management and treatment.

Apparatus

- pH meter: pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of NaOH and HCl
- Beakers

Reagents

- **Buffer solution of 4.0 pH (Thallate buffer):** 10.2 grams of potassium hydrogen thallate was dissolved in one litter double distilled water.
- **Bufer solution of 7.0 pH (Phosphate buffer):** 3.4 gram of borax was dissolved in one liter double distilled water.
- **Buffer solution of 9.2 pH (Borax Buffer):** 3.81 gram of borax was dissolved in one liter of double distilled water.

Procedure

1. After calibration with buffer solution, rinse the electrode with DDW and wipe gently.
2. Take the sample in a beaker. Bring the temperature of the sample to room temperature.
3. Deep the electrode in the beaker in such a way that bulb of the electrode deep in to sample. Bring the temperature to homogeneity by stirring.
4. Record the reading from display which will give the pH value of the sample.

Calculation

The read out of the pH meter will gives direct pH value of the sample.

5.3.3 Electrical conductivity (EC)

EC is an important parameter to assess the wastewater quality. It is a measure of ionic concentration. It is an indicator of salinity also and measured in mS/cm.

Apparatus

The EC of effluent was estimated using conductivity meter.

Reagents

Standard KCL solution: The EC meter was calibrated with standard KCL solution (0.1N). The standard KCL solution of 0.1N was prepared by dissolving 0.747 gm of

KCL (AR grade) in 100 ml double distilled water. The EC of standard solution was set at 12.88 mmho cm^{-1}. After calibration of instrument, EC of sample was recorded.

5.3.4 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(17th edition).

5.3.5 Estimation of BOD

BOD was estimated as per standards method No. 5210 B, page No.5-4 from STANDARD METHODS for the examination water and wastewater, 1989(17th edition).BOD was estimated by BOD bottle method.

5.3.6 Total dissolved solids (TDS)

TDS were estimated as per the standards methods No. 2540 C, page No.2-74 of STANDARD METHODS for the examination of water and wastewater.

5.3.7 Total suspended solids (TSS)

TSS was estimated by method No. 2540 D, page No. 2-75 of STANDARDS METHODS for the examination of water and wastewater.

5.3.8 UV intensity measurement

UV intensity was measured in the UV reactor with the help of radiometer. Radiometer was placed at different places from top with variation in distance from UV tubes such as top of the reactor, bottom of the reactor and middle of the reactor. It has been observed that the maximum UV intensity was at the middle of the UV reactor which was measured to be 25 W/m^2.

5.4 Photocatalytic Treatment

Photocatalytic treatment was done for Pharmaceutical effluent sample. The effluent of Pharmaceutical industry were treated and the various parameters like pH, catalyst dose, concentration of oxidant are optimized.

5.4.1 Degradation of Pharmaceutical effluent

Wastewater collected from the homogenous tank of effluent treatment plant (ETP) of Chemical and Pharmaceutical industry was untreated wastewater highly polluted and its characteristics are shown in Table 4.1. So to get the value within measurable range, sample was diluted twice. Single distilled water was used for the all dilutions. Initial pH of sample was checked and varied all the parameter to optimize the value of pH, catalyst dose, oxidant concentration and comparison of photocatalytic activity with solar light. 200 ml of sample taken in glass bowl (1000ml quantity) and bowl was covered with transparent thin foil; air is also supplied by the aerator during experiments. Wastewater sample was treated in the presence of UV light in photo reactor for seven hours. Sample was withdrawn in every 1 hr., filtered through the syringe filter and absorbance was taken in spectrophotometer. COD of samples was measured as per the standard methods. All tests were repeated for getting the reproducibility of results.

After the photocatalytic and solar photocatalytic treatment of wastewater (with optimized conditions), sample was filtered and it has been analyzed for COD, TSS, TDS, Color pH, EC, Turbidity etc.

CHAPTER-6

RESULTS AND DISSCUSSIONS

The photocatalytic treatment using TiO_2 catalyst was employed for the effective degradation of Chemical and Pharmaceutical wastewater in batch photo reactor at 298 K. A matrix of experimental variables was developed in which the TiO_2 dose, pH, UV exposure time and use of oxidant were varied and applied to Chemical & Pharmaceutical wastewater.

6.1 Treatment of Chemical & Pharmaceutical Waste Water

Chemical and Pharmaceutical industry generate large amount of wastewater, which is a toxic chemical having high COD value. Chemical and Pharmaceutical wastewater includes a large variety of chemicals addition that makes the environmental challenge for Chemical and Pharmaceutical not only as liquid waste but also in its chemical composition. The Chemical and Pharmaceutical processes require the input of a wide range of chemicals which are generally organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in pharmaceutical wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble (*Vincenzo et al., 2007, A. A. Kdasl et. al., 2004*).

6.1.1 Characteristics of Wastewater

Raw wastewater sample was collected from homogenous tank of Chemical and Pharmaceutical Industry. Firstly sample was analyzed for some initial parameters. The values of various wastewater parameters before treatment are shown in Table 6.1

Table 6.1 Characteristics of Wastewater from Pharmaceutical Industry

S. No.	Parameter	Value
1.	pH	2.98
2.	EC (mS/cm)	6.73
3	Temperature(^{o}C)	38
4.	Turbidity (NTU)	2.2
5.	TSS (mg/l)	50
6.	TDS (mg/l)	1270
7.	COD (mg/l)	8000
8.	BOD (mg/l)	2800

These wastewater parameters presented in above table shows that wastewater is highly polluted. So treatment of wastewater is required to facilitate the biological treatment processes and disposal of water into surface water body within the specified disposable limits.

The industrial effluent has high color value and it has show also peaks through absorption spectra. Peak obtained in UV region shows the presence of different organic and chromophoric compounds as shown in Fig6.1.1.

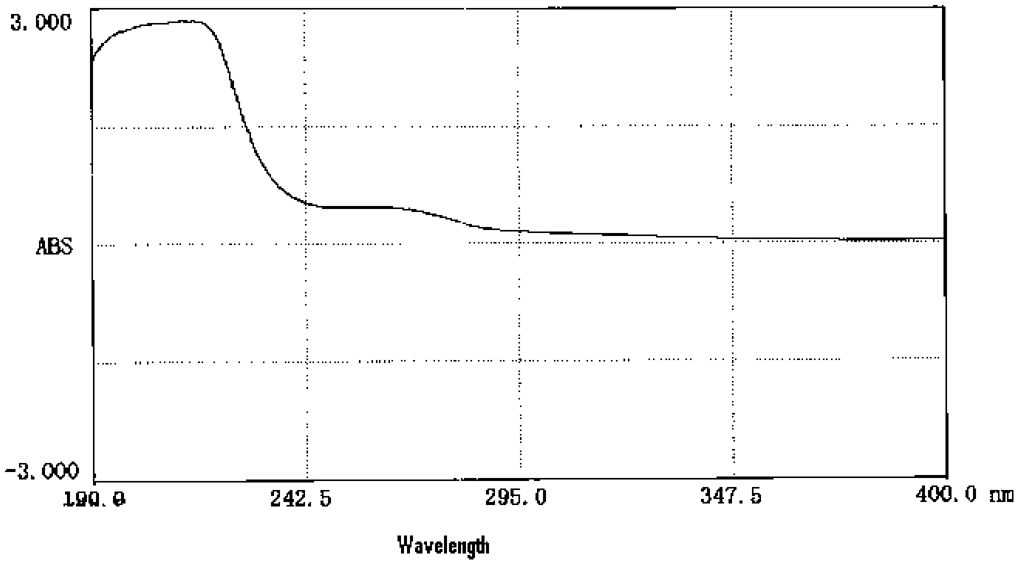
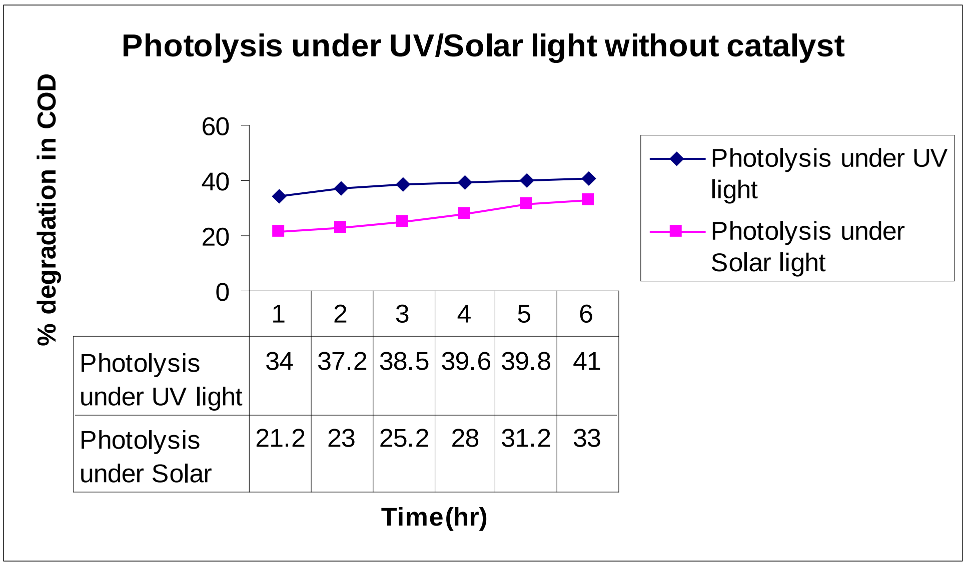


Fig- 6.1 Absorption spectra of Chemical and Pharmaceutical effluent

6.1.2 Photolysis of chemical & Pharmaceutical Waste Water

Pharmaceutical wastewater was irradiated under ultraviolet (UV) and solar light alone in the absence of catalyst, as shown in fig.6.2. It was observed that after 6 hr treatment the Pharmaceutical waste water is not significant result in COD degradation. *M. Faisal et. al., 2005; W.S.Kuo and P.H.Ho, 2006* have reported the similar behaviour during the photolysis of textile effluent under ultraviolet irradiation.

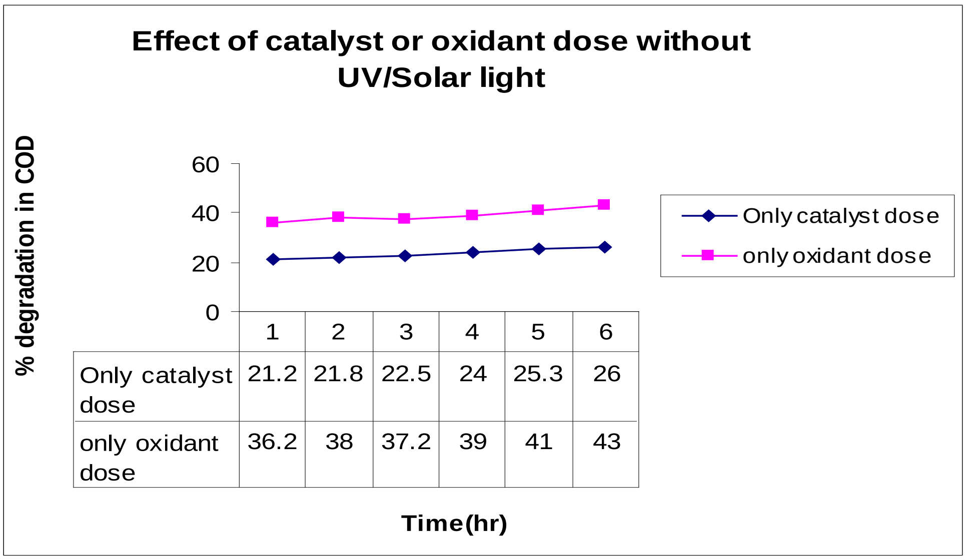


	1	2	3	4	5	6
Photolysis under UV light	34	37.2	38.5	39.6	39.8	41
Photolysis under Solar	21.2	23	25.2	28	31.2	33

Fig-6.2 Effect of UV/ Solar light only, Time= 6 hr.

6.1.3 Treatment of wastewater with catalyst or oxidant(without light source)

Wastewater was subjected to treatment with TiO_2 catalyst as well as $Ca(OCl)_2$ oxidant in the absence of light source. The result shown in fig.6.3 shows the no significant reduction in COD was obtained after 6 hrs. of treatment.



	1	2	3	4	5	6
Only catalyst dose	21.2	21.8	22.5	24	25.3	26
only oxidant dose	36.2	38	37.2	39	41	43

Fig-6.3 Effect of catalyst and oxidant dose without UV/Solar light,Time=6 hr

6.1.4 Influence of Initial pH

pH plays an important role in photocatalytic oxidation processes because pH affects the production of hydroxyl radical which is powerful oxidizing agent. Pharmaceutical industry generate wastewater with a low pH value 2.98 which was collected from homogenous tank of effluent treatment plant. So pH of the sample was varied from 2.0 to 10 at 3g/l of catalyst dose during experimentation and it was found that with increasing pH there is decrease in degradation rate. The maximum degradation of 90.6% was observed at pH 4.0 and the final pH after photocatalytic treatment was 7.56 which is suitable for biological treatment as well as discharge of wastewater into the water bodies.

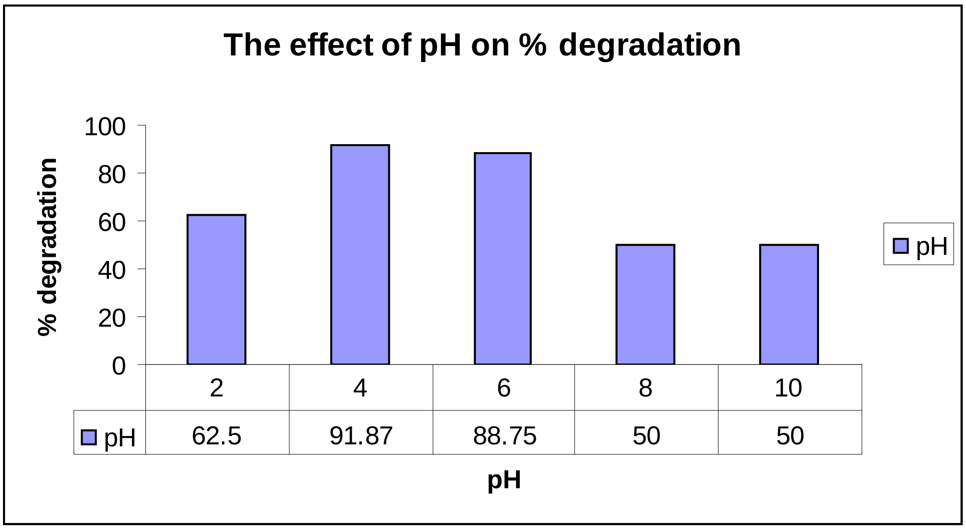


Fig-6.4 Effect of initial pH on photocatalytic degradation of pharmaceutical Effluent [TiO_2]=3g/l, Irradiation time=7hr.

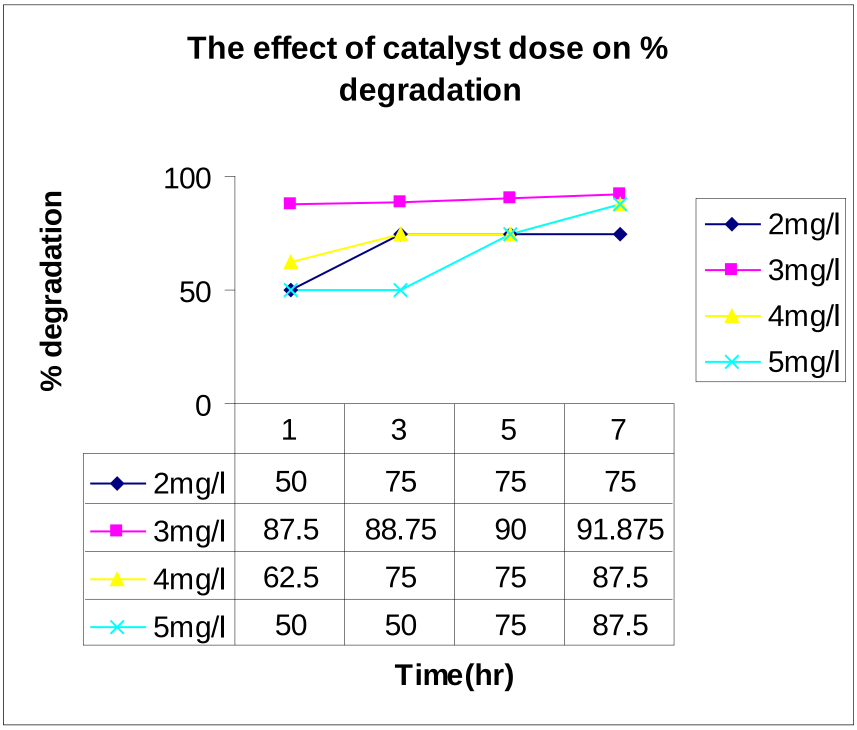
Literature survey it has been found that operating pH of solution significantly affects catalyst activity. *Isil Akmehmet Balcioglu et al. (2004)* studied the effect of pH in the range 2-7 for the degradation of simulated pharmaceutical plant effluent and it is observed that lowering the pH of simulated pharmaceutical plant effluent, significantly improved the COD removal efficiency.

6.1.5 Variation of Catalyst (TiO_2) Dose

The catalyst dose is an important parameter which has strong influence on the degradation kinetics of Pharmaceutical effluent. Degussa P-25 TiO_2 catalyst was used in slurry mode. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of TiO_2 varying from

2g/L to 5g/L, at optimized pH of 4 and results are presented in Fig-6.4. The graph show that as the concentration of catalyst increases from 2g/l to 5g /L, the percentage degradation increases from 50% to 91.8% but increasing the catalyst concentration from 4 to 5g/L, the percentage degradation decreases from 91.8% to 50% respectively. So maximum degradation rate has been observed with catalyst dose of 3g/L and it was considered as the optimum dose for the degradation of chemical and Pharmaceutical effluent for subsequent analysis.

The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. When all the molecules are adsorbed on TiO_2 no improvement is achieved by adding more catalyst. The decrease in efficiency, which is observed in the figure, may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of TiO_2 particles. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of TiO_2 which makes a significant fraction of catalyst to be inaccessible to either absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction.



	1	3	5	7
2mg/l	50	75	75	75
3mg/l	87.5	88.75	90	91.875
4mg/l	62.5	75	75	87.5
5mg/l	50	50	75	87.5

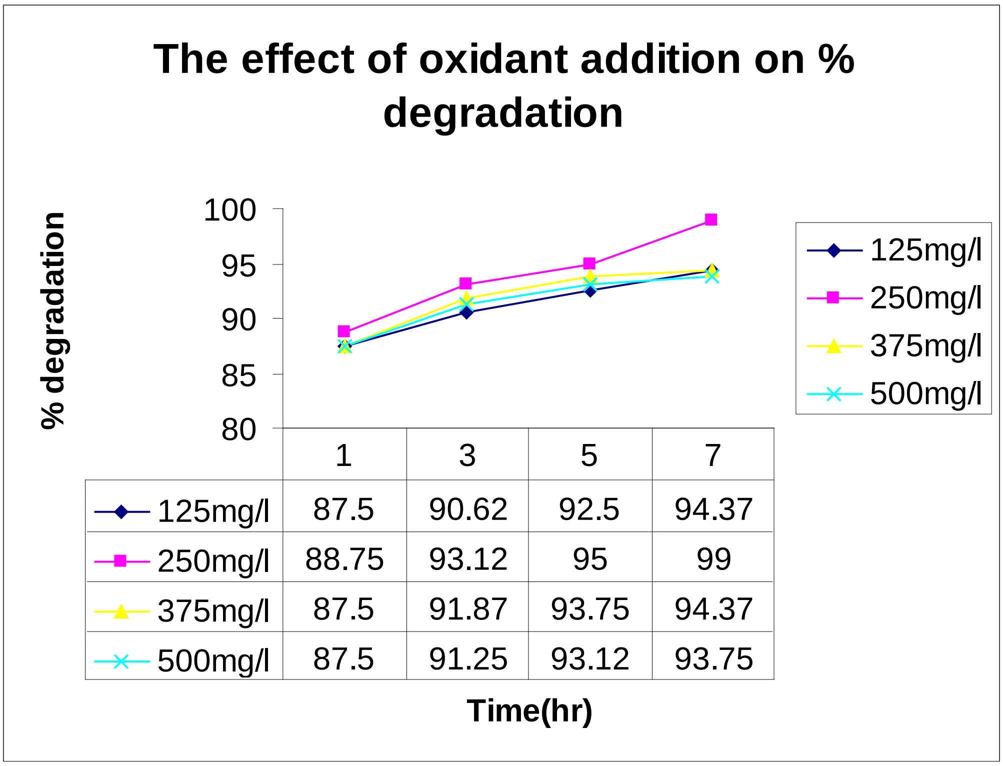
Fig-6.5 Effect of catalyst dose on photocatalytic degradation of Pharmaceutical effect [pH] = 4.0, Irradiation time=7hr.

C. G. Silva et. al., 2006 has reported that degree of degradation increases with the increasing amount of catalyst concentration up to a certain limit and beyond after that further increase in catalyst dose degradation has been decreased.

6.1.6 Effect of Oxidant Dose

One possible way to increase the reaction rate is to increase the concentration of $^{\cdot}OH$ radicals because these species are promoters of photocatalytic degradation. For the degradation of wastewater $Ca(OCl)_2$ was used as an oxidant alongwith $TiO_{2.}$ The concentration of oxidant was varied from 125ml/l to 500ml/l at fixed TiO_2 dose (3.0g/l) and at constant pH (4.0) during experimentation. Results obtained shows that the degradation rate increases from the 87.5% to 99%. It is clear from the figure that the maximum percentage degradation 99 % was obtained at 250 ml/L of $Ca(OCl)_2$ dose and it has been taken as optimum amount required for the maximum effective treatment of pollutants. The rate of photocatalytic degradation of wastewater is significantly improved with increase in calcium hypochlorite concentration and reached to a maximum value, beyond which increasing $Ca(OCl)_2$ dose retards the degradation (Fig. 6.6). This dual effect of $Ca(OCl)_2$ can be explained by radical reaction mechanisms. By addition of excess $Ca(OCl)_2$, it acts as hydroxyl radical or hole scavenger to form the per hydroxyl radicals ($HO_2^{\bullet}$) which is a much weaker oxidant than hydroxyl radicals.

Therefore, high concentration of calcium hypochlorite inhibited the degradation reaction rate by competing with wastewater for available hydroxyl radicals. A similar observation has been found that an increase in $Ca(OCl)_2$ level enhanced degradation rate up to an optimum concentration beyond which, inhibition occurs and organic pollutant (*S.K. Dubey, 2006; S. S. Reddy et. al., 2005; M.A.Behnajady et. al., 2005; M. Muruganandham et. al., 2005*).



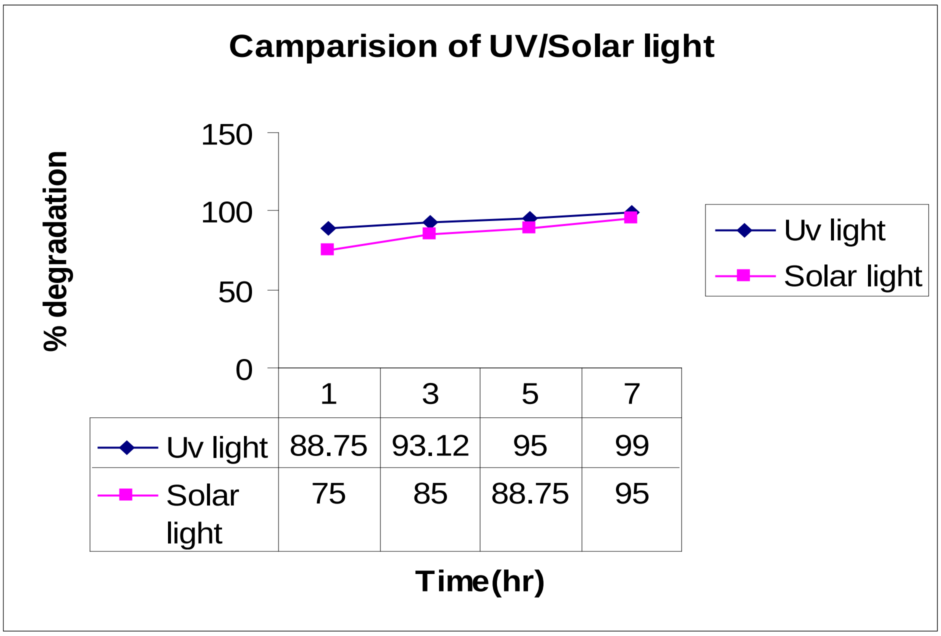
	1	3	5	7
◆ 125mg/l	87.5	90.62	92.5	94.37
■ 250mg/l	88.75	93.12	95	99
▲ 375mg/l	87.5	91.87	93.75	94.37
× 500mg/l	87.5	91.25	93.12	93.75

Fig- 6.6 Effect of $Ca(OCl)_2$ concentration on photocatalytic degradation of Pharmaceutical effluent. $[TiO_2]$ = 3.0 g/l, pH=4.0.

6.1.7 Comparison of Solar/UV Light

The effect of light source on the degradation of wastewater by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of effluent in Solar/UV as well as normal room light. The aqueous suspensions of TiO_2 (3 mg/L)containing 200ml effluent was exposed to Solar, UV and normal room conditions at pH 4.0. Fig- 6.7 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of effluent under sunlight, visible and UV light source, respectively. The rate of degradation was found to be slightly more in the UV light in comparison to solar light. After 7hr of reaction time the percentage degradation was 95% in solar light and 99% in UV light. 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.

This is due to their ability to absorb part of the visible light, another mechanism of degradation connected with visible light could occur as well. According to this mechanistic approach, the adsorbed chemical molecule onto the TiO_2 surface form appropriate excited states due to visible illumination and then these excited states mainly transfer electrons to the conduction band of TiO_2 particles.



	1	3	5	7
Uv light	88.75	93.12	95	99
Solar light	75	85	88.75	95

Fig- 6.7 Effect of UV/Solar light on photo catalytic degradation of effluent at 4 pH & [TiO_2] = 3.0 g/l.

M. Faisal et. al., 2005 studied the aqueous suspensions of TiO_2 containing dye derivatives acridine orange and ethidium bromide to solar radiation. It was found that the degradation of the model compounds proceeds much more rapidly in the presence of UV light source as compared to sunlight. *M. Muruganandham et. al., 2006* studied the Solar/TiO_2 process for photo catalytic decolorization of Reactive Yellow 14 dye which was completely decolorized in 80 min. *W.S. Kuo et. al., 2006* identified the application of TiO_2 film to solar photocatalysis of organic dyes, including methylene blue, RR195 and RY145. It was found that after 6-h solar irradiation, in case of TiO_2 film the degradation capability of solar photocatalytic system was significantly improved without TiO_2 film.

6.1.8 Effluent Characteristics after Photocatalytic Treatment

After the photocatalytic treatment of effluent under optimized conditions i.e. at TiO_2 dose of 3.0 g/l and operating pH of 4.0, in UV light characterization of the treated wastewater was done. Table- 6.2 shows the parameters analyzed after the 7 hrs of photocatalytic treatment of wastewater which depicts a major reduction in pollution load. This results shows that complete degradation of organic compounds in wastewater has occurred. The other parameters like COD, TDS and EC as examined after treatment shows the 99% reduction in COD, 60% TDS reduction after 7 hrs of reaction time. In the presence of solar light COD reduction was found to be 95 %, TDS reduction was 66% after 7 hrs of treatment. Electrical conductivity has been observed to increase

Table 6.2 Characteristics of Wastewater after Photocatalytic (UV) Treatment Under Optimized Condition

S. No.	Parameter	Before Treatment	After Treatment	% Reduction
1.	pH	2.98	7.56	--
2.	TSS (mg/l)	50	14	72
3.	TDS (mg/l)	1270	350	72
4.	COD (mg/l)	8000	80	99
5.	BOD(mg/l)	2800	30	98.92

Table 6.3 Characteristics of Wastewater after Solar Photocatalytic Treatment Under Optimized Condition

S. No.	Parameter	Before Treatment	After Treatment	% Reduction
1.	pH	2.98	8.03	--
2.	TSS (mg/l)	50	20	60
3.	TDS (mg/l)	1270	390	69
4.	COD (mg/l)	8000	400	95
5.	BOD(mg/l)	2800	130	95

CHAPTER-7

CONCLUSION

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. Photocatalytic process is expensive due to application of UV light and catalyst. India, being a tropical country, has plenty availability of sunlight so solar photocatalysis is an attractive and cost effective option for the application of this technology at industrial scale.

Treatment of Chemical and Pharmaceutical wastewater has been carried out with variation in parameters like pH, catalyst dose, oxidant $Ca(OCl)_2$ concentration and comparison of Solar/UV light. Degradation observed was 99% under optimized conditions i.e. 4.0 pH, catalyst concentration of 3.0 g/l and oxidant dose of 250ml/l after 7hrs of treatment in UV light.. In the presence of solar light, 95% degradation has been achieved after 7hrs of reaction time same conditions. It has been observed that after 7 hours of photocatalytic treatment, COD reduction of 99%, TDS reduction of 70% and 72% of TSS reduction occurs. COD reduction shows in the degradation of organic compounds present in wastewater. Turbidity reduction helps to increase photosynthetic activity in aquatic system and total solids reduction enhances the capability of recycling and reuse of wastewater after treatment.

The reduction in COD of effluent in the UV and solar photocatalytic treatment shows the complete degradation of organic compounds into simpler end products which results in the complete mineralization of resulting solutions.

The important parameters like COD, TSS, TDS, pH have been compared with the National Environmental Quality Standards (NEQS) and it is evident from the results that end pH was 7.56 which is neutral. COD of the photocatalytic treated sample 80 mg/l in UV light which is well within the prescribed COD standard(250 mg/l) for the discharge of the effluent. While COD of the treated effluent in solar light was 400 mg/l which somewhat higher than the prescribed limit. Hence, it can be concluded from the observations that solar photocatalysis can be suitably and cost effectively employed for the degradation of pharmaceutical waste water with little more retention time.

The results of solid analysis depicts great reduction in TDS and TSS of the effluent.TDS was reduced from 1270 mg/l to 350 mg/l & 390 mg/l in UV & Solar light respectively. TSS was observed to reduced from 5o mg/l to 14 mg/l and 20 mg/l which also meets the standard for safe discharge of wastewater. Hence it can be concluded that heterogeneous photocatalyst can be efficiently employed for the degradation of pharmaceutical wastewater along with natural solar light with little more retention time.

REFERENCES

Abdullah, M., Low, G.K. and Matthews, R.W., "Effects of Common Inorganic Anions on Rates of Photocatalytic Oxidation of Organic Carbon over Illuminated Titanium Dioxide," *J. Phys. Chem*., **94**, 6820 (1990).

Alaton, I. and Balcioglu, I. (2002) "The effect of pre-ozonation on the H_2O_2/UV treatment of raw and biological pre-treated textile industry wastewater", *Water Sci. Technol.,* **45**: 297-304.

Alinsafi A., Evenou F., Abdulkarim E.M., Zahraa M.N. P., Benhammou A., Yaacoubi A. and Nejmeddine A., (2007), "Treatment of textile industry wastewater by supported photo catalysis", *Dyes and Pigments***,** **74**, 439-445.

Andreozzi, R., Caprio, V., Insola, A. and Marotta, R. (1999) "Advanced Oxidation Processes (AOP) for water purification and recovery", *Catalysis Today,* **53**: 51-59.

Arcand-Hoy, L.D., A.C. Nimrod, and W.H. Benson, ''Endocrine- Modulating Substances in the Environment Estrogenic Effects of Pharmaceutical Products'', *Int. J. Toxicol*., **17(2)**:139–158 (1998).

Attaia A. J., Kadhim S. H. and Hussien F. H., (2008), "Photocatalytic degradation of textile dyeing wastewater using titanium dioxide and zinc oxide", *E-Journal of Chemistry*, **5**: 219-223.

Augugliaro V, Ciardelli G, Corsi L, García-López E, Loddo V, Marcí G, Palmisano L and Schiavello M. (2001)," Photocatalytic degradation of actual textile industrial wastewater in aqueous suspensions of polycrystalline TiO_2", *Ann Chim*., **92**: 761-70.

Balanosky, E., Fernandez, J., Kiwi, J. and Lopez, A. (1999) "Degradation of membrane concentrates of the textile industry by Fenton like reactions in iron-free solutions at biocompatible pH values", *Water Sci. Technol.,* **40**: 417-424.

Balcioglu, I. and Arslan, I. (2001) "Partial oxidation of reactive dyestuffs and synthetic textile dye-bath by the O_3 and O_3/H_2O_2 processes", *Water Sci. Technol*. **43**: 221-228.

Belfroid, A.C., A. Van der Horst, A.D. Vethaak, A.J. Scha¨ fer, G.B.J. Rijs, J. Wegener, and W.P. Cofino, ''Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and waste water in The Netherlands'' *Sci. Total Environ.,* **225(1–2):**101–108 (1999).

Benkelberg, H. and Warneck, P. (1995) "Photodecomposition of iron (III) hydroxo and sulfate complexes in aqueous solution. Wavelength dependence of OH and SO^{4-}quantum yields", *J. Phys. Chem*., **99**: 5214-5221.

Bigda, R. (1995) "Consider Fenton's chemistry for wastewater treatment", *Chem. Eng. Progr.,* **91**: 62-66.

Boyd, G.R., H. Reemtsma, D.A. Grimm, and S. Mitra, ‘‘Pharmaceuticals and Personal Care Products (PPCPs) in Surface and Treated Waters of Louisiana, USA and Ontario, Canada’’, *Sci. Total Environ.*, **311(1–3)**:135–149 (2003).

Brand, N., Mailhot, G. and Bolte, M. (1997) “Degradation and photodegradation of tetraacetylethylenediamine (TAED) in the presence of Iron (III) in aqueous solution”, *Chemosphere,* **84**: 2637-2648.

C.G.Silva, W.Wangand J.L.Faria (2006), “Photocatalytic and photochemical degradation of mono-,di-,and tri-azo dyes in aqueous solution under UV irradiation”,**xxx**,xxx-xxx.

C.C. Chena, Chung-S. L., Y.C. Chung (2005), “Photocatalytic degradation of ethyl violet in aqueous solution mediated by TiO_2 suspensions”, *Journal of Photochemistry and Photobiology A: Chemistry*,**xxx**, xxx–xxx.

Cahill, J.D., E.T. Furlong, M.R. Burkhardt, D. Kolpin, and L.G. Anderson, ‘‘Determination of Pharmaceutical Compounds in Surface- and Ground-Water Samples by Solid-Phase Castiglioni, S., R. Fanelli, D. Calamari, R. Bagnati, and E. Zuccato, ‘‘Methodological Approaches for Studying Pharmaceuticals in the Environment by Comparing Predicted and Measured Concentrations in River Po, Italy’’, *Regul. Toxicol. Pharmacol.,* **39(1):**25–32 (2004).

Caliman A. F; Teodosiu C; and Balasanian I; (2002), “applications of heterogeneous photocatalysis for industrial wastewater treatment”, *Environmental Engineering and Management,* **1**, 187-196.

Chamarro, E., A., M. and Esplugas, S. (2001) “Use of Fenton reagent to inprove organic chemical biodegradability”, *Wat. Res.,* **35**: 1047-1051.

Chen, H.Y., Zahraa, O. and Bouchy, M., “Inhibition of Adsorption and Photocatalytic Degradation of an Organic Contaminant in Aqueous Suspension of TiO_2 by Inorganic Ions,” *J. Photochem. & Photobio. A: Chem.,* **108**: 37 (1997).

Chin-Chuan L., Yung-Hsu H., P., C.-H. Li and C.-L. Kao (2006**), “**Photodegradation treatment of azo dye wastewater by UV/TiO_2 process”, *Dyes and Pigments* , **12**: 191-195

Clara, M., B. Strenn, and N. Kreuzinger, ‘‘Carbamazepine as a Possible Anthropogenic Marker in the Aquatic Environment: Investigations on the Behaviour of Carbamazepine in Wastewater Treatment and During Groundwater Infiltration’’, *Water Res.,* **38(4):**947–954 (2004).

Contreras, S., Rodríguez, M., Chamarro, E., Esplugas, S. and Casado, J. (2001) “Oxidation of nitrobenzene by O3/UV: The influence of H_2O_2 and Fe(III). Experiences in a pilot plant”, *Water Sci. Technol.,* **44**: 39-46.

Cun Wang , X., Bo-Qing X., J., Bixian M., P., Guoying S. and Jiamo F. (2004), “Enhanced photocatalytic performance of nanosized coupled ZnO/SnO_2 photocatalysts for methyl orange degradation”, *Journal of Photochemistry and Photobiology A: Chemistry*, **168**: 47–52.

Curco, D., Malato, S., Blanco, J., Gimenez, J. and Marco, P. (1996b) “Photocatalytic degradation of phenol: comparison between pilot-plant-scale and laboratory results”. *Solar Energy*, **56**: 387-400.

De Laat, J., Gallard, H. and Legube, B. (1999) “Comparative study of the oxidation of atrazine and acetone by H2O2/UV, Fe(III)/UV, Fe(III)/H_2O_2/UV and Fe(II) or Fe(III)/H2O2”, *Chemosphere,* **39**: 2693-2706.

Debska, J., A. Kot-Wasik, and J. Namies´nik, ‘‘Fate and Analysis of Pharmaceutical Residues in the Aquatic Environment’’, *Crit. Rev. Anal. Chem.*, **34(1):**51–67 (2004). 42.

Doll, T.E. and F.H. Frimmel, ‘‘Removal of Selected Persistent Organic Pollutants by Heterogeneous Photocatalysis in Water’’, *Catal. Today*, **101(3–4):**195–202 (2005c).

E. Bizani K. Fytianos, I. Poulios , V. Tsiridis (2006), “Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide”, *Journal of Hazardous Materials* **xxx**, xxx–xxx.

Extraction and High-Performance Liquid Chromatography-Electrospray Ionization Mass Spectrometry’’, *J. Chromatogr*. A, **1041(1–2):**171–180 (2004).

Faust, B. and Hoigne, J. (1990) “Photolysis of Fe(III) - hydroxy complexes as sources of OH radicals in clouds, fog and rain”, *Atmos. Environ,* **24A**: 79-89.

Fenton, H. (1894) “Oxidation of tartaric acid in presence of iron”, *J. Chem. Soc. Trans.*, **65**: 899-910.

G. Boyd, H. Reemtsma, A. Grimm, S. Mitra, S. *The Sci. of the Total Environ*. 311, 135-149 (2003).

Gallard, H., De Laat, J. and Legube, B. (1999) “Spectrophotometric study of the formation of iron(III)-hydroperoxy complexes in homogeneus aqueous solutions”, *Wat. Res.*, **33**: 2929-2936

García, J., Diez, F. and Coca, J. (1989) “Métodos alternativos para el tratamiento de efleuntes fenólicos industriales” , *Ingenieria Química*, **238**: 151-158.

Ghozzi K., Zayani G, Bousselmi L. and Ghrabi A. (2002), “Comparison of efficiency of two solar-catalytic systems treatment of textile dyes and washing out reagents”, *Proceedings of International Symposium on Environmental Pollution Control and Waste Management*, 683-87.

Gimenez, J., Curco, D., Malato, S. and Blanco, J. (1996) “Photocatalysis and radiation absorption in a solar plant”, *Solar Energy Materials and Solar Cells*, **44**: 199-217

Glaze, W. and Chapin, D. (1987) “The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation”, *Ozone Sci. & Eng.*, **9**: 335-342.

Glaze, W. and Kang, J. (1989) “Advanced oxidation processes. Test of a kinetic model for the oxidation of organic compounds with ozone and hydrogen peroxide in a semibatch reactor”, *Ind. Eng. Chem. Res*., **28**: 1580-1587.

Guittonneau, S., Glaze, W., Duguet, J. and Wable, O. (1991) “Characterization of natural waters for potential to oxidize organic pollutants with ozone”, *Proc. 10th Ozone World Congress*, Zürich, Switzerland

Haber, F. and Weiss, J. (1934) “The catalytic decomposition of hydrogen peroxide by iron salts”, *J. Proc. Roy. Soc*. London A, **147**: 332-351.

Halling-Sørensen, B., S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C.H. Lu¨ tzhøft, and S.E. Jørgensen, ‘‘Occurrence, Fate and Effects of Pharmaceutical Substances in the Environment—A Review’’ *Chemosphere,* **36(2):**357–394 (1998).

Hartig, C., M. Ernst, and M. Jekel, ‘‘Membrane Filtration of Two Sulphonamides in Tertiary Effluents and Subsequent Adsorption on Activated Carbon’’, *Water Res.,* **35(16):**3998–4003 (2001).

Heberer, T., ‘‘Occurrence, Fate, and Removal of Pharmaceutical Residues in the Aquatic Environment: A Review of Recent Research Data’’, *Toxicol. Lett*., **131(1–2):**5–17 (2002).

Hirsch, R., T. Ternes, K. Haberer, and K.L. Kratz, ‘‘Occurrence of Antibiotics in the Aquatic Environment’’, *Sci. Total Environ*., **225(1–2):**109–118 (1999).

Hu C. and Wang Y. (1999),” Decolorization and biodegradability of photo catalytic treated azo dyes and wool textile wastewater”, *Chemosphere*, **39**: 2107-15.

IIT, CHENNI (2001) Organized,” *UNESCO Regional Training Programme in Environmental Chemistry*”, Pages- 36-39.

Isil Akmehment Balcio_Glu, Merih ¨otker, “Pre-Treatment of Antibiotic Formulation Wastewater by O_3, O_3/H_2O_2, and O_3/UV Processes” *Turkish J. Eng. Env. Sci.* 28 (2004) , 325 – 331.

Jian-Hui S. , S., Jing-Yu S., R., Li-Ping Q., H. and Mao-Hong F. (2006), “Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation”, ultrasonic sono., **14**, 761-766.

Jones, O.A., J.N. Lester, and N. Voulvoulis, ‘‘Pharmaceuticals: A Threat to Drinking Water?’’, *Trends Biotechnol*., **23(4):**163–167 (2005a).

Joshi P, Purohit J and Neti N.R.(2001), “Photocatalytic degradation of reactive dyes and simulated dye bath wastewater”, *Water Sci Technol.*, **43**:313-320.

Jun Wang , W., Zhaohong Zhang , Z., Rui Xu , Y., and Xiangdong Z. (2007) ,“Treatment of nano-sized rutile phase TiO_2 powder under ultrasonic irradiation in hydrogen peroxide solution and investigation of its sonocatalytic activity”, *ultrasonic sonochemistry*,**xxx**,xxx.

Kaludjerski, M. (2001) “Enhancement of biodegradability of dichlorodiethyl ether by preoxidation”, *Master of Science Thesis, San Diego State University* ,CA, USA.

Kang, S., Liao, C. and Po, S. (2000) “Decolorization of textile wastewater by photo-fenton oxidation technology”, *Chemosphere*, **41**: 1287-1294.

Kdasl A. A., idris A.K; Saed C. T; Gaun (2004), “Treatment of textile wastewater by advanced oxidation processes – A Review”, *Global Nest: the Int*. J., 6, 222-230.

Kolpin, D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, and H.T. Buxton, ‘‘Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance’’, *Environ. Sci. Technol.*, **36(6):**1202–1211 (2002).

Ku¨ mmerer, K., ‘‘Resistance in the Environment’’, *J. Antimicrob. Chemother.*, **54(2):**311–320 (2004).

Ku¨mmerer, K., ‘‘Drugs in the Environment: Emission of Drugs, Diagnostic Aids and Disinfectants into Wastewater by Hospitals in Relation to Other Sources — A Review’’, *Chemosphere,* **45(6–7):**957– 969 (2001).

Larsen, T.A., J. Lienert, A. Joss, and H. Siegrist, ‘‘How to Avoid Pharmaceuticals in the Aquatic Environment’’, *J. Biotechnol.*, **113(1–3):**295–304 (2004).

Lee, J. C., Kim, M. S., Kim, C.K., Chung, C.H., Cho, S. M., Han, G.Y., Yoon, K. J. and Kim, B.W. “Removal of Paraquat in Aqueous Suspension of TiO2 in an Immersed UV Photoreactor,” *Korean J. Chem. Eng.,* **20(5):** 862 (2003).

Lipczynska-Kochany, E. (1992) “Degradation of nitrobenzene and nitrophenols by means of advanced oxidation processes in a homogeneous phase: Photolysis in the presence of hydrogen peroxide versus the Fenton reaction”, *Chemosphere*, **24**: 1369-1380.

M. Blesa, B. Sanchez, *Eliminación de contaminantes por fotocatalisis heterogénea. CIEMAT. Madrid* (2004).

Mowery HR and Loganathan BG,(2006), “Persistent organic compounds in wastewater :Azithromyci and urobilin concentration in wastewater treatment plant samples from ,Murry ,USA.” , Department of Chemistry and Center for Reservoir Research

M. Faisal M. Abu Tariq and M. Muneer (2005), “Photocatalyzed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania”, *Dyes and Pigments*, x**xx,** 1-7.

M.A. Behnajady, N.Modirshahla and R. Hamzavi (2005),“kinetic study on photocatalytic degradation of C.I. acid yellow 23 by ZnO photocatalysis”, *Journal of hazardous material*, xxx, xxx-xxx.

M. Carballa, F. Omil, J. Lema, M. Llompart, C. García-Jares, I. Rodríguez, M. Gómez, T. Ternes. *Water Res*. **38**: 2918-2926 (2004).

M. Haque, M Muneer. *Journ of Haz. Mat.* **145**: 51-57 (2007)

Mazellier, P., Bolte, M. (1999) “ Primary mechanism for the iron (III) photoinduced degradation of 4-chlorophenol in aquoes solution”, *New J. Chem*., 133-135.

Mazellier, P., Bolte, M. (2001) “ 3-chlorophenol elimination upon excitation of dilute iron (III) solution: evidence for the only involvement of $Fe(OH)^{2+}$”, *Chemosphere,* **42**:361-366.

Miao, X.S., F. Bishay, M. Chen, and C.D. Metcalfe, ‘‘Occurrence of Antimicrobials in the Final Effluents ofWastewater Treatment Plants in Canada’’, *Environ. Sci. Technol*., **38(13):**3533–3541 (2004).

Minero, C., Pelizzetti, C., Piccini, P. and Vinceti, M. (1994) “Photocatalyzed transformation of nitrobenzene on TiO2 and ZnO”, *Chemosphere*, **28**: 1229-1244.

Minero, C., Pelizzetti, E., Malato, S. and Blanco, J. (1993) “Large solar plant photocatalytic water decontamination - degradation of pentachlorophenol”, *Chemosphere*, **26**: 2103-2119.

Mokrini, A., Oussi, D. and Esplugas, S. (1997) “Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide” , *Water Sci. Technol.*, **35**, 95-102.

Naresh N. Mahamuni and Aniruddha B. Pandit (2006), “Effect of additives on ultrasonic degradation of phenol”, *Ultrasonic Sonochemistry*, **13**, 165–174.

Na, Y. S., Kim, D.H., Lee, C.H., Lee, S.W., Park, Y. S., Oh, Y. K., Park, S.H. and Song, S.K., “Photocatalytic Decolorization of Rhodamine B (RhB) by Fluidized Bed Reactor with Hollow Ceramic Ball Photocatalyst,” *Korean J. Chem. Eng.*, **21(2):** 430 (2004).

Nansheng, D., Tao, F. and Shizhong, T. (1996) “Photodegradation of dyes in aqueous solutions containing Fe(III)--hydroxy complex I. Photodegradation kinetics”, *Chemosphere*, **33**: 547-557.

Ne´stor J. B.-P. and Marco F. S.-H. (2007), “Sonophotocatalytic degradation of congo red and methyl orange in the presence of TiO_2 as a catalyst”, *Ultrasonics Sonochemistry*, **14**: 589–595.

Nghiem, L.D., A. Manis, K. Soldenhoff, and A.I. Schafer, ‘‘Estrogenic Hormone Removal from Wastewater Using NF/RO Membranes’’, *J. Membr. Sci.*, **242(1–2):**37–45 (2004).

Nghiem, L.D., A.I. Schafer, and M. Elimelech, ‘‘Pharmaceutical Retention Mechanisms by Nanofiltration Membranes’’, *Environ. Sci. Technol*., **39(19):**7698–7705 (2005).

Nigam, P., Banat, I. M., Singh, D. and Marchant, R., “Microbial Process for the Decolorization of Textile Effluent Containing Azo/Diazo and Reactive Dyes,” *Process Biochemistry,* **31(5):** 435 (1996).

Niyaz Mohammad M., M., Nargess Y. L. and Nooshin S. T. (2006), “Kinetics of heterogeneous photo catalytic degradation of reactive dyes in an immobilized TiO_2 photocatalytic reactor”, *Journal of Colloid and Interface Science*, **295**: 159–164.

O. Gonzalez, C. Sans, S. Esplugas. Jour. Haz. Mat. **146**: 459-464 (2007).

Pekakis PA, Xekoukoulotakis NP and Mantzavinos D.(2006),” Treatment of textile dye house wastewater by TiO_2 photocatalysis”, *Water Res.* ,**40**:1276-86.

Perez, M., Torrades, F., Domenech, X. and Peral, J. (2002) “Fenton and photo-Fenton oxidation of textile effluents”, *Wat. Res*., **36**: 2703-2710.

Peyton, G. and Glaze, W. (1988) “Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone”, *Environ. Sci. & Technol*., **22**: 761-767.

Putschew, A., S. Wischnack, and M. Jekel, ‘‘Occurrence of Triiodinated X-ray Contrast Agents in the Aquatic Environment’’, *Sci. Total Environ*., **255(1–3):**129–134 (2000).

R. Comparelli, E. Fanizza , M.L. Curri , P.D. Cozzoli ,G. Mascolo and A. Agostiano (2005), “UV-induced photocatalytic degradation of azo dyes by organic-capped ZnO nanocrystals immobilized onto substrates”, *Applied Catalysis B: Environmental,* **60:** 1–11.

R. Torres, C. Pétrier, E. Combet, M.Carrier, C. Pulgarin. Ultrason. Sonochem. Corrected Proof, Avail. online 28 July 2007.

Ramesh Thiruvenkatachari, Saravanamuthu Vigneswaran and Il Shik Moon," UV/TiO2 photocatalytic oxidation process”, *Korean J. Chem. Eng*., **25(1):** 64-72 (2008).

Richardson, M.L. and J.M. Bowron, ‘‘The Fate of Pharmaceutical Chemicals in the Aquatic Environment’’, *J. Pharm. Pharmacol*., **37(1):**1–12 (1985).

Ruppert, G., Bauer, R. and Heisler, G. (1993) “The photo-Fenton reaction - an effective photochemical wastewater treatment process”, *J. Photochem. Photobiol. A*, **73**: 75-78.

S. Parson (ed), Advanced oxidation process for water and wastewater treatment. *IWA publishing. London* (2004).

S. Richards, S. Cole. Ecotoxicology. **15**: 647-65 (2006).

S. S. Reddy and B. Kotaiah (2005), "Decolorization of simulated spent reactive dye bath using solar / TiO_2 / H_2O_2", *Int. J. Environ. Sci. Tech*. **2:**245-251**.**

Sacher, F., F.T. Lange, H.J. Brauch, and I. Blankenhorn, ''Pharmaceuticals in Groundwaters—Analytical Methods and Results of a Monitoring Program in Baden-Wurttemberg, Germany'', *J. Chromatogr*. A, **938(1–2):**199–210 (2001).

Safarzadeh-Amiri, A., Bolton, J. and Cater, S. (1996) "Ferrioxalate-mediated solar degradation of organic contaminants in water", *Solar Energy*, **56**: 439-443.

Shashi Kant Dubey (2006), "solar photo catalytic treatment biodegradability enhancement (heterogeneous)". *M.Tech. Thesis*, *Thapar University, patiala*, 12-18.

Snyder, S.A., P. Westerhoff, Y. Yoon, and D.L. Sedlak, ''Pharmaceuticals, Personal Care Products, and Endocrine Disruptors in Water: Implications for the Water Industry'', *Environ. Eng. Sci*., 20(5):449–469 (2003).

Soulet, B., A. Tauxe, and J. Tarradellas, ''Analysis of Acidic Drugs in Swiss Wastewaters'', *Int. J. Environ. Anal. Chem*., **82(10):**659– 667 (2002).

Stackelberg, P.E., E.T. Furlong, M.T. Meyer, S.D. Zaugg, A.K. Henderson, and D.B. Reissman, ''Persistence of Pharmaceutical Compounds and Other Organic Wastewater Contaminants in a Conventional Drinking-Water Treatment Plant'', *Sci. Total Environ*., **329(1–3):**99–113 (2004).

Sumpter, J.P., ''Xenoendocrine Disrupters — Environmental Impacts'', *Toxicol. Lett.*, **102–103**:337–342 (1998).

Sun, Y. and Pignatello, J. (1993). "Photochemical-reactions involved in the total mineralization of 2,4-D by Fe3+/H2O2/UV", *Environ. Sci.& Technol*., **27**: 304-310.

Sychev, A. Y. and Isak, V. G. (1995) "Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O2 and H2O2 and of the ativation of organic substrates", *Russian Chemical Reviews*, **64**: 1105-1129.

T. Doll, F.H. Frimmel. *Wat. Res***. 38**: 955-964 (2004).

Ternes, T.A. and R. Hirsch, ''Occurrence and Behavior of X-ray Contrast Media in Sewage Facilities and the Aquatic Environment'', *Environ. Sci. Technol*., **34(13):**2741–2748 (2000).

Ternes, T.A., ''Occurrence of Drugs in German Sewage Treatment Plants and Rivers'', *Water Res*., **32(11):**3245–3260 (1998).

Ternes, T.A., M. Meisenheimer, D. McDowell, F. Sacher, H.J. Brauch, B.H. Gulde, G. Preuss, U. Wilme, and N.Z. Seibert, ‘‘Removal of Pharmaceuticals During Drinking Water Treatment’’, *Environ. Sci. Technol*., **36(17):**3855–3863 (2002).

Ternes, T.A., M. Stumpf, J. Mueller, K. Haberer, R.D. Wilken, and M. Servos, ‘‘Behavior and Occurrence of Estrogens in Municipal Sewage Treatment Plants—I. Investigations in Germany, Canada and Brazil’’, *Sci. Total Environ*., **225(1–2):**81– 90 (1999).

Trapido, M., Veressinina, Y. and Kallas, J. (2001) “Degradation of aqueous nitrophenols by ozone combined with UV-radiation and hydrogen peroxide*”, Ozone Sci. & Eng.*, **23**: 333-342.

Vincenzo, L, Despo, C., Giusy and A., Vincenzo (2007), “Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse”, *desalination*, **215**, 166-176.

W.S. Kuo and P.H. Ho (2006),”Solar photo catalytic decolorization of dyes in solution with TiO_2 film”, *Dyes and Pigments*, **71**, 212-217.

Walling, C. (1975) “Fenton's reagent revisited”, *Acc. Chem. Res*., **8**: 125-131.

Wang, K.H., Hsieh, Y.H., Wu, C.H. and Chang, C.Y., “The pH and Anion Effects on the Heterogeneous Photocatalytic Degradation of o-Methyl Benzoic Acid in TiO2 Aqueous Suspension,” *Chemosphere*, **40**: 389 (2000).

Yingxu C. , S., Kan W.and Liping L. (2005), “Role of primary active species and TiO_2 surface characteristic in UV-illuminated photo degradation of Acid Orange 7”, *Journal of Photochemistry and Photobiology A: Chemistry*, **172** :47–54.

Youji Li., Junwen L. and Jing Y. (2005), “Photocatalytic degradation of methyl orange in a sparged tube reactor with TiO_2-coated activated carbon composites”, *Catalysis Communications*, **6** ,650–655.

Young Soo Na, Chang Han Lee, Tae Kyung Lee, Song Woo Lee, Young Seek Park*, You Kwan Oh, Sung Hoon Park and Seung Koo Song†’, “Photocatalytic Decomposition of Nonbiodegradable Substances in Wastewater from an Acrylic Fibre Manufacturing Process*”, Korean J. Chem. Eng*., **22(2):** 246-249 (2005)

Z. Zainal , L. K. Hui, M. Z. Hussein, Y. H. Taufiq-Yap, A. H. Abdullah, I. Ramli (2005),“Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps”, *Journal of Hazardous Materials* B, **125**: 113–120.

Zepp, L., Faust, B. and Hoigné, J. (1992) “Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction”, *Environ. Sci.& Technol*., **26**: 313-319.