Photocatalytic Degradation of Pharmaceuticals Wastewater

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CERTIFICATE

I hereby declare that the thesis entitled **"Photocatalytic degradation of pharmaceuticals wastewater"** is an authentic record of my work carried out as requirements for the award of the degree of **Master of Technology** in **Chemical Engineering** at **Thapar University, Patiala** under the supervision of **Dr. V. K. Sangal**, Associate Professor, Chemical Engineering Department, Thapar University, Patiala. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

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It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

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ABSTRACT

Heterogeneous photocatalysis process has proved its superiority to other conventional methods of wastewater treatments in the presence of biorecalcitrant compounds. In the present study the heterogeneous photocatalytic degradation for the pharmaceutical compound Ornidazole and real wastewater from pharmaceutical industry with TiO_2 was assessed. The investigation of % degradation of Ornidazole using TiO_2 as a photo catalyst was done. The experiments were conducted in slurry mode and fixed mode. The input parameters which were varied were pH, Ornidazole concentration, TiO_2 dose and time. ANN was applied for the modeling of the photocatalytic process. Optimization was performed by using RSM with desirability approach. The experiments were performed at the optimized conditions for slurry mode and fixed mode using TiO_2 immobilized on cement beads. At the optimum conditions the % degradation was found to be 77.7% for slurry mode and for fixed bed the % degradation was 76.5% for 360 min. The results showed that the predictions agreed with the experimental results. Kinetic study showed that degradation of ornidazole follows the second order kinetics.

The investigation of % COD removal of real pharmaceutical waste water using TiO_2 as a photo catalyst was done. The experiments were conducted in slurry mode. The input parameters which were varied were pH, TiO_2 dose and time. Optimization was performed by using RSM with desirability approach. The experiments were performed at the optimized condition. At the optimum conditions the % COD removal was found to be 63.7%. The results showed that the predictions agreed with the experimental results. Kinetic study shows that degradation of real wastewater follows the second order kinetics.

Bioassay testing was conducted for the treated wastewater. The treated wastewater was found to be non toxic and could be disposed off to the environment safely.

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ABBREVATIONS USED

- AOPs- Advanced Oxidation Processes
- AOT-Advanced Oxidation Technologies
- APIs- Active pharmaceutical ingredients
- BBD- Box-Behnken Design
- cm - Centimetres
- cm^2 - Square centimetres
- cm^3 - Cubic centimetres
- E_g - Band gap energy
- eV - Electron volts
- e_{cb}^- electron (conduction band)
- eq- Equation
- Fig- Figure
- ft - feet
- g - Gram
- g^{-1} - per gram
- GC-MS - Gas Chromatography Mass Spectroscopy
- GHG - Green Houses Gases
- GJ - Gigajoules
- h_{vb}^+- holes(valance band)
- HPLC - High Performance Liquid Chromatography
- hr^{-1} - per hour
- ID - Inner Diameter
- IUPAC - International Union of Pure and Applied Chemistry
- i.e.- That is
- Kg - Kilogram
- L - litre
- L^{-1} - per litre

- LED - Light-emitting Diode
- m - Metres
- M - Moles
- *m/z* - mass to charge ratio
- m^2 - Meters square
- m^3 - Meters cubic
- mg - Milligram
- min^{-1} - Per minute
- μL - Microlitre
- mL - Millilitre
- μm - Micrometres
- μmol - Micro moles
- mM - Milli moles
- mm - Millimetres
- nm - Nanometres
- ^oC - Degrees Celsius
- OD - Outer Diameter
- OH^- - Hydroxyl ion
- $OH^\bullet$- Hydroxyl radical
- ppm - Parts per million
- PPs- Pharmaceutical Products
- PPCP-Pharmaceutical and personal care products
- PC- Photocatalysis
- RSM-Response Surface Methodology
- TiO_2- Titanium Oxide
- TDS—Total Dissolved Solids
- TS- Total Solids
- TSS- Total Suspended Solids
- UV- Ultraviolet
- WWTP-Waste Water Treatment Plant

CHAPTER 1

INTRODUCTION

1.1 General

Water is essential requirement of all domestic, industrial and commercial activities, so the wastewater generated from different activities contains a variety of contaminants which are harmful for both flora and fauna existing on this planet. The industrial operations comprise primarily textile, pharmaceutical, pesticides and other organic chemicals manufacturing industries generate wastewater having various pharmaceutical drugs and other components. Humans have recognized the fact, but disregard it by polluting rivers, lakes, and oceans. Subsequently, it is harming our planet to the point where organisms are dying at a very alarming rate.

1.2 Contaminant of concern in wastewater treatment

The major contaminants of concern in wastewater treatment are suspended solids, pathogens, biodegradable organics, heavy metals, dissolved inorganics etc. Secondary treatment standards for wastewater are concerned with the removal of biodegradable organic, suspended solids, and pathogens. Many of the more severe standards that have been developed recently which deal with the removal of priority pollutants.

1.3 Pharmaceuticals as a pollutant

Pharmaceuticals with different physicochemical and biological characteristics and functionalities have been largely consumed over the last 50 years. These compounds are most notably characterized by their more or less specific biological activity and low mocro-biodegradability feature. Most of the pharmaceutical drugs are discarded in their original chemical structures or metabolites through toilet (human only can metabolize a little percentage of the medicines), or production facilities, hospitals, and private household into the municipal sewers. Pharmaceutical products containing active pharmaceutical ingredients (APIs), although being originally created as drugs to treat a variety of ailments in humans and animals, have in fact turned out to have negative environmental impact due to their too much use and consequent occurrence in groundwater, urban wastewater, surface water and also drinking water. Among the numerous available APIs on the market, an environmentally important group of pharmaceuticals includes beta-blockers (β-blockers), antibiotics, nonsteroidal anti-inflammatory drugs, anti epileptics, antidepressants, blood lipid lowering agents, hormones, antihistamines and X-ray contrast media. The presence and concentration levels of these compounds are still not known properly due to its complex structure but continuing ingestion of these compounds in drinking water is serious issue. Fig 1.1 shows the origin of PPs and the pathways by which these pharmaceutical compounds (waste) enter into environment and in water cycle. Development of resistance in pathogenic bacteria, aquatic toxicity, endocrine disruption, genotoxicity etc are some hazards caused by pharmaceutical compounds.

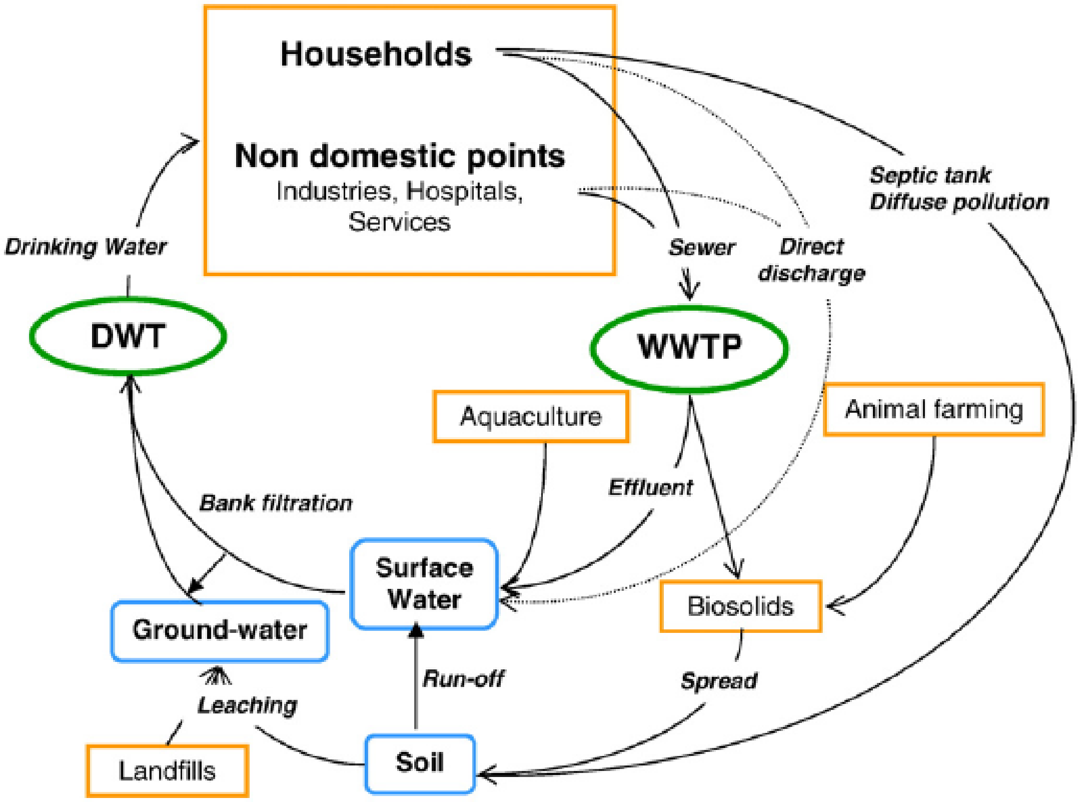


Fig1.1: Origin and routes of Pharmaceutical Products (Source: Petrovic et al. 2003)

Others from solid waste landfill or manure waste could enter into the water cycle, due to their non-adsorbed polar structure. The traditional wastewater treatment plants are typically not designed to deal with polar micro-pollutants such as pharmaceuticals. With the respect of pharmaceutical characteristic being resistant to microbial degradation, low removal percentages are performed in the secondary treatment in traditional water treatments. Such final effluents containing residual pharmaceuticals are discharged into natural surface water bodies.

When discharged from hospitals, households, industries and pharmacies, these pharmaceuticals may enter wastewater treatment plants (WWTPs). Due to the considerable variation in physico-chemical properties of pharmaceuticals and the configuration of WWTP facilities, the treatment efficiency can vary significantly requiring a broad range of removal protocols (Halling-Sorensen et al. 1999, Ternes 1998). The non-biodegradable characteristics and relatively high solubility of the APIs renders conventional chemical and biological treatments futile, thus leading to an increased occurrence of the parent drugs and their metabolites into both the aquatic and terrestrial environments. Veterinary medicines are also known to directly increase APIs levels in the soil and groundwater. Consequently, their concentrations, which are commonly reported in trace levels (ng/*l* to µg/*l*), have the potential to harm terrestrial and aquatic organisms. Hence, APIs have been recognized as important environmental pollutants necessitating the search for effective technologies to reduce their increasing concentration in the environment.

Unfortunately, some of these pharmaceuticals are not totally removed by WWTPs. Recent studies demonstrated that conventional treatment plants, largely based on the use of microorganisms, are insufficient to effectively devastate organic compounds, due to their intricate molecular structure and low concentrations in the water, and that the percentage of compound removed can be lower than 10%.

There are currently no legally regulated maximum permitted concentrations of pharmaceuticals in the environment, despite their unknown impact on the environment and human health. On the precaution principle, the European Union Water Framework Directive produces an updated list of priority substances every four years (2000/60/EC) and has identified compounds from pharmaceuticals as potential pollutants. Polluted water can generally be treated effectively by biological treatment plants, using adsorbents or conventional chemical treatments (chlorination, ozonation, or permanganate oxidation). However, these treatments are occasionally not competent of degrading pollutants to the required levels by law or essential for the subsequent use of the effluent. Antiprotozoal and antibacterial agents have limited activity against aerobic bacteria. They comprise a family of antibiotics that have been utilized in veterinary and human medicine to treat ailments caused by protozoans and bacterial infections.

1.4 Wastewater discharge standards for pharmaceutical industries

As environmental regulations become more stringent, a suitable treatment of effluent is required 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 1.1

Table 1.1: National Environmental Quality Standards (NEQS) of Pharmaceutical Effluent

	Parameter	**Concentration not to exceed limits in mg/*l***
Compulsory	pH	6.5-8.5
Additional	Oil & Grease	10
	BOD(3 days at 27^{O}C)	100
	COD	250
	Total Suspended Solids	100
	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 according to CPCB standard

1.5 Conventional technologies

In general, WWTPs comprise a primary system of physicochemical treatments and a secondary system that consists of a biological reactor formed by activated sludge.

1.5.1 Physio-chemical treatment

Other treatment processes have been examined with the aim of finding relevant techniques to diminish concentrations of pharmaceuticals in wastewater. These comprise membrane processes, AC (activated carbon). A number of types of membrane and applications were assessed for the removal of APIs, including different techniques of filtration such as ultra filtration, microfiltration, nanofiltration, electrodialysis reversal, reverse osmosis, combinations of different membranes in series and membrane bioreactors (Bellona & Drewes 2007,Toth et al.

2011). Activated carbon is a majorly used conventional technology for the removal of both synthetic organic contaminants and natural compounds. It is mainly used as granular form in packed bed filters or in form of powdered feed (Singh et al. 2011). In conventional filters Granular activated carbon (GAC) could be used as a replacement of anthracite media, providing both filtration and adsorption. However, disposal and carbon regeneration are environmental considerations. Normally, physico-chemical treatment techniques like adsorption processes, membrane filtration, and chemical coagulation are not favoured for the removal of such kind of drugs due to costly adsorbents, membranes cleaning, chemical coagulants and formation of large amount of sludge. The common processes related with hydrolysis, sewage treatment, biodegradation and sorption are futile for the degradation of many pharmaceuticals (Gartiser et al. 2007). Thus AOPs might be the dominant technologies in transformation of antibiotics in the environment.

1.5.2 Biological treatment methods

They have conventionally used for the treatment of pharmaceutical wastewater .Biological method consists of anaerobic processes and aerobic processes. Aerobic applications comprise membrane batch reactors, activated sludge and sequence batch reactors (Raj and Anjaneyulu. 2005,Noble. 2006 and Chang et al. 2008). Anaerobic methods comprise anaerobic film reactors anaerobic sludge reactors and anaerobic filters (Oktem et al. 2007, Sreekanth et al. 2009). Conventional activated sludge with a high retention time has been employed for the treatment of pharmaceutical industry wastewater (Oz et al. 2004). In general, it doesnot cause any impact to environmental and has a lower capital cost than more advanced methods for treatment and only a limited operational requisite is needed. However, the production of large amounts of sludge high energy consumption and operational problems including foaming, color and bulking in secondary clarifiers are associated with AS plants (Sreekanth et al. 2009). The impact of pharmaceuticals on the Activated Sludge process appears to be negligible under normal operating conditions.

In brief, conventional treatment methods are not capable to completely remove a large amount of the organic micropollutants present in urban wastewaters. More effectual and specific treatment methods are required to decrease the environmental and potential impact of effluents and comply with increasingly strict legislation. Degradation of these nonbiodegradable organic compounds is not possible by conventional biological treatment processes so, advanced oxidation processes (AOPs) are of major interest now days as AOPs not only remove organic and inorganic pollutants but also effectively decrease toxicity along with complete mineralization.

CHAPTER 2

ADVANCED OXIDATION PROCESSES (AOP’s)

2.1 Introduction

AOPs are very efficient in the oxidation of organic and inorganic compounds. Free radicals formation is a basic of this process notably the hydroxyl radical ($OH^\bullet$), highly reactive species that can effectively attack most organic molecules. These radicals can generate numerous systems, making AOPs highly versatile (Andreozzi 1999 ,Esplugas et al. 2007).

Among all the water treatment technologies, Advanced Oxidation Processes (AOPs) present a great potential for effectively treating a very wide range of emerging contaminants, such as pharmaceuticals. AOPs are all based on the in-situ generation of short-lived highly reactive oxygen species with low selectivity such as hydroxyl radicals ($HO^\bullet$), O_3 and superoxide anion radical ($O_2^{\bullet-}$), ideally providing pathways for the organic compounds to complete mineralization to CO_2, H_2O and inorganic ions or acids. Commonly applied photochemical technologies (e.g. UV, UV/ H_2O_2) and increasingly popular photocatalytic oxidation (e.g. UV/TiO_2) processes both aiming at pollutant abatement, mineralization and improvement of biodegradability, have been actively investigated for water treatment to remove pharmaceuticals. Direct and indirect photochemical degradation protocols have been reported to be efficient to degrade various APIs. The ability of most APIs to undergo direct photolysis may be limited by the poor light absorption by the target compound. Recently, photocatalytic oxidation, in particular with semiconductor titanium dioxide (TiO_2) has found increasing attention in water purification. This process, which offers the advantage to operate at mild (ambient) temperature and pressure as well as permitting the use of sunlight as irradiation source has demonstrated to be efficient in the removal of pharmaceuticals from water.

2.2 Theoretical background of advanced oxidation processes (AOPs)

Free radical species and reactive oxygen represents highly efficient oxidants that can initiate AOPs to mineralize organic and inorganic to nontoxic and simpler molecules. Free radical species are containing one or more electrons which are unpaired such as the hydroperoxyl radical ($HO_2^\bullet$) or alkoxyl radical ($RO^\bullet$), superoxide anion radical ($O2^{\bullet-}$), hydroxyl radical ($HO^\bullet$), with the $HO^\bullet$ radical species attracted the attention. The characteristic features of $HO^{\bullet}$ radicals are high reactivity, non-selective nature and powerful oxidizing species. They are ranked second to fluorine and are able to attack a wide range of organic contaminants. Reactions of $HO^{\bullet}$ radicals with pollutant particles can be either by hydrogen abstraction (Eq. 1) from C-H, N-H, or O-H bonds, radical-radical interactions. For example, the addition of molecular O_2 leading to the formation of peroxyl radical (Eq. 2), or through direct electron transfer (Eq 3) producing oxidized intermediates and after complete mineralization, produced CO_2, H_2O and inorganic acids.

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \tag{1}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{2}$$

$$HO^{\bullet} + RX \rightarrow RX^{\bullet +} + HO^{-} \tag{3}$$

Despite the high oxidation potential, kinetic rates of interaction with $HO^{\bullet}$ radicals and organic components depend on the affinity of these compounds towards the oxidant. Considerable amounts of work have been published pertaining to the investigation of potential AOPs or the abatement of pharmaceuticals in water. Applications of AOPs for wastewater treatment in general have been reviewed including specific applications of AOPs to pharmaceutical treatment. Recent representative studies carried out in this area for the degradation of pharmaceuticals are presented in summarized and highlighted selected works of different AOPs treatment on pharmaceuticals from 1997-2008. AOPs are commonly applied for pharmaceutical wastewater treatment (Andreozzi 1999,Esplugas et al. 2007). Table 2.1 shows most commonly used advanced oxidation process .It is divided in two parts i.e. photochemical and non photochemical processes. Combinations of the processes given below could also be used.

Table 2.1: Ordinary AOT evaluated for water and wastewater treatment

Photochemical processes	Non-photochemical processes
UV oxidative process	O_3, O_3/ H_2O_2
UV/H_2O_2	Fenton reagent
UV/O_3	Ultrasound
UV/ H_2O_2 /O_3	US/ H_2O_2, US/O_3, US/Fenton

UV/Ultrasound	Electrochemical oxidation
Photo-Fenton	Supercritical water oxidation
Photocatalysis	Ionizing radiation
Sono photocatalysis	Electron-beam irradiation
Vacuum UV (VUV)	Wet-air oxidation
Microwave	Pulsed plasma

Source: (Gultekin and Ince 2007)

2.3. Photochemical degradation

The International Union of Pure and Applied Chemistry (IUPAC) define photodegradation as “the photochemical alteration of a molecule into simpler and lower molecular weight fragments, usually involving an oxidation process. The ultimate goal of applying photochemical degradation techniques, which are based on light from either artificial or natural source, is to destroy pollutants and ultimately complete mineralization to carbonate species (CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}), water and mineral acids (HX).

Photochemistry is the backbone of all photochemical reactions and photochemical transformations is governed by two basic principles:

a) Grotthus-Draper law (First law of photochemistry): Electromagnetic radiation that is absorbed by a molecule leads to a distinct photochemical change

b) Stark-Einstein law (Second law of photochemistry): Each molecule that takes part in a photochemical reaction absorbs one quantum of light energy.

Although these two principles are significant in photochemistry, the beginning of photochemistry as a new field of investigation was the initiated by Giacomo Ciamician and Paul Silber, who studied the interaction of light with matter between 1900 and 1915.

2.3.1 Homogeneous photodegradation: Photolysis

Photolysis is the interaction of natural or artificial UV radiation with the molecule of interest and can lead to split in to intermediate products and simultaneously total mineralization occur. This photo-induced process are direct or indirect. Direct photolysis takes place when an organic compound, C, absorbs light to form an excited state (C*) which can then decompose as illustrated below (Eq. 4):

$$C + h\nu \rightarrow C^* \rightarrow \text{Degradation products} \qquad (4)$$

UV/H_2O_2 is also a direct method to generate $HO^\bullet$ radicals through homolytic cleavage of H_2O_2, as shown below (Eq. 5):

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \qquad (5)$$

Photolysis is compound dependent and the absorption of light by pharmaceuticals can be expressed by the Beer-Lambert law. Nevertheless, not all APIs are sensitive to this process. Laboratory-scale photodegradation provides the flexibility to choose the appropriate light source based on the absorption spectrum of the pharmaceutical of interest (Doll & Frimmel 2003). Solar UV-B $280<\lambda<315$ nm and part of UV-A $315<\lambda<400$ nm are known to induce photochemical reactions (direct and indirect) in surface waters, while the visible range is not efficient in initiating direct photolysis of most organic compounds. Pharmaceuticals with chromophores that can absorb light >290 nm in sunlight can possibly undergo direct photolysis. For compounds with absorption <290 nm, indirect photolysis by singlet oxygen (O_2), alkyl peroxy radicals ($^\bullet OOR$) and hydroxyl ($HO^\bullet$) can be initiated naturally by photolysis of nitrate, nitrite and chromophoric dissolved organic material present in natural water (Doll & Frimmel 2003). The presence of natural organic matter, including humic substances ubiquitously in aquatic environment, are able to produce high ROS such as O_2, superoxide and $HO^\bullet$ radicals, but can also act as a radical scavenger leading to a decrease in photodegradation of pharmaceuticals.

2.3.2 Heterogeneous photodegradation: Photocatalysis

The IUPAC definition given for photocatalysis is an alteration in the rate of a chemical reaction and its initiation under the action of UV, visible or IR in the presence of a photocatalyst that absorbs light and chemical transformation of the reaction partners takes place. The goal of the photocatalytic processes is not only the removal of organic pollutants, but at the same time for complete mineralization. Semiconductors or insulators consist of a valence band (vb) filled by electrons and a conduction band (cb) unoccupied or only partly occupied with electrons. For the semiconductors, electronic transitions between vb and the cb require at least UV/Vis irradiation with equivalent energy to the band-gap energy (E_g). Semiconductor materials with E_g>2 eV are also referred to as wide band gap semiconductors, due to the energy requirement of near UV radiation or visible light. Selected examples of wide band gap semiconductors are presented in Table 2.2. Various semiconductors such as CdS, ZnO, TiO_2, Fe_2O_3 and WO_3 (pistokova et al. 2015; Prieto-Rodriguez et al. 2012; Fukahori and fujiwara, 2015; Sarkar et al. 2015) can be activated with minimum wavelength of UV or VIS radiation as shown in Table 2.2. Among various semiconductor materials tested under similar conditions for the degradation of organic components, TiO_2 has been preferred as most active photocatalyst.

Table 2.2: Band gap energy and minimum wavelength for selected photocatalysts

Semiconductor	E_g (eV)	λ_{nm}	Radiation type
TiO_2 (anatase)	3.2	388	UV
TiO_2 (rutile)	3.0	413	VIS
ZnO	3.2	387	UV
ZnS	3.6	344	UV
Fe_2O_3	2.3	539	VIS
WO_3	2.7	459	VIS

(Bhatkhande et al. 2002)

The properties of TiO_2 accounting for its wide use as a photocatalyst are due to its high photorectivity, low cost, low toxicity, chemical stability over a wide pH range, commercial availability and its resistance to photo-corrosion (Bouna et al. 2013). Besides these advantages, atmospheric O_2 can be used as oxidant and only long wavelength of UV light (UV-A) is required for the photocatalyst activation. In addition, it is possible to drive the process with solar light. TiO_2 suspensions in water cause its surface to be hydroxylated. The hydroxyl groups act as a source of powerful $HO^\bullet$ radicals, which get oxidized various organic components reached to mineralization to CO_2 and other mineral acid (Turchi 1990). Intermediates formed due to partial oxidation of orignal compound may possibly impact the reaction rates negatively by competing for adsorption sites on the TiO_2 surface or display a higher toxicity than the original compound. To evaluate complete mineralization, parameters such as TOC and DOC for evolution of CO_2 are commonly measured.

2.4. Photocatalyst features of titanium dioxide

Three crystalline forms of TiO_2 exist, namely brookite, rutile and anatase. Anatase is commonly using as active photocatalyst (Hoffmann et al. 1995). The Combinations of rutile and anatase also showed better photocatalytic activity, due to the promotion of charge pair separation and inhibition of electron-hole pair recombination. In contrast, brookite TiO_2 is known to be rare and difficult to prepare, which contributes to its neglected usage in photocatalysis, although studies have been performed with this form. In fact, a recent study indicated higher photocatalytic activity of brookite compared to anatase and rutile. The extensive use of TiO_2 Degussa P25 as a photocatalyst in photocatalytic degradation studies is attributed to its morphology or crysallities. Being a mixture of 20% rutile and 80% anatase its high surface area and a particle size of 20-30 nm are the characteristic features responsible for the performance of TiO2 P25 in photocatalytic applications. The anatase form tends to be the highly photoactive and stable form at temperature $<700^0$C. Anatase and brookite are, thermodynamically meta-stable (silva et al. 2009). Different TiO_2 materials demonstrate different photocatalytic activity towards similar organic compounds even under identical conditions. Explanations of such differences are differences in porosity, crystal phase, surface charge, specific surface area, morphology, surface hydroxyl density control, band gap and particle size distribution. Other commonly used photocatalysts besides TiO_2 P25, include Hombicat UV 100 and Ti (IV) oxide (Aldrich).

2.5. General mechanism of TIO_2 photocatalysis

The most commonly used TiO_2 form is anatase, with band gap energy (BGP) of 3.2 eV (Table 2.2). Photon (*hv*) illumination ($380<\lambda<400$ nm) occurs onto the TiO_2 surface of more than or equal to the BGP. This follows electron excitation and promotion from the valence band of semiconductor to the conduction band of it. The e^- and h^+ pairs involved in oxidative and reductive reactions with molecules present near the semiconductor surface is shown in

Fig.2.1.

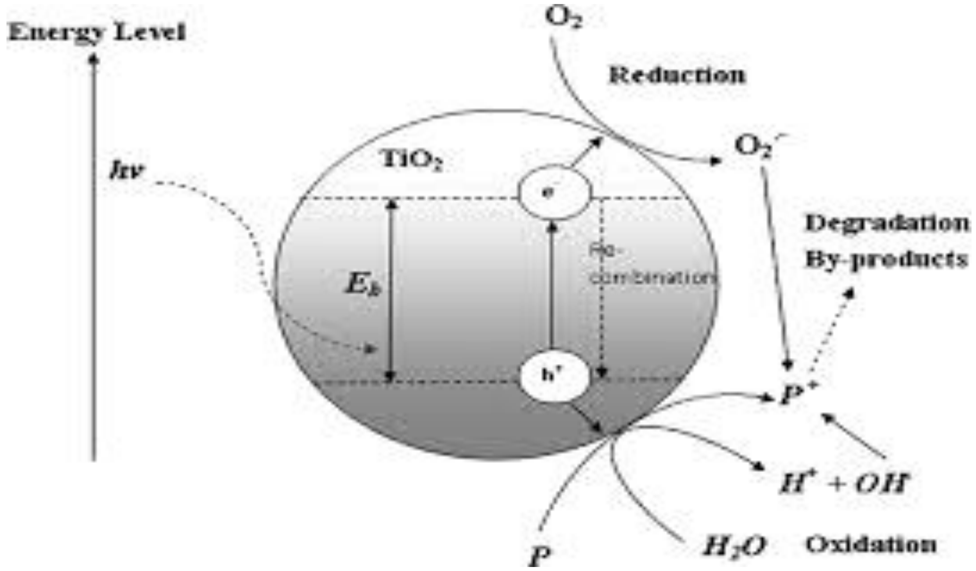


Fig 2.1: Photocatalytic processes on TiO_2 semiconductor (Umar & Aziz 2013)

The degradation ability of inorganic and organic pollutants comes from the redox reaction undergoing after photo–activation of the semiconductor material. Titanium dioxide in it, the highest occupied energy band is called valence band and the lowest empty band is called conduction band. Band gap separated these bands by which in the order of electron volts. When a higher energy photon or equal to the band–gap value of TiO_2 is absorbed by particle, an electron from the valence band is promoted to the conduction band with simultaneously generation of a photogenerated hole (h_{vb}^+) in the valence band and photogenerated electron (e_{cb}^-) in the conduction band. The general mechanism of the hydroxyl–radical intermediates formed in photocatalytic reaction process is represented by Eqs. 6–11. TiO_2 Anatase exhibits greater photocatalytic activity due to its conduction band position which shows stronger reducing power. The initial step for photocatalytic degradation is formation of highly reactive but short time–lived hydroxyl radical ($OH^\bullet$) by hole trapping. The $OH^\bullet$ is formed on the extremely hydroxylated semiconductor surface. This process is immediately followed by the depletion of adsorbed oxygen species, which is obtained from dissolved oxygen molecules, or by other electron acceptors available. The h_{vb}^+ and the e_{cb}^-can reunite in the bulk or on the surface of the particle in very few nanoseconds (Eq. 11) or can be confine in surface states and then react with donor or acceptor species adsorbed or close to the particle surface. Then, the redox reactions can be initiated. The hole of valence band is highly oxidizing and the electron of conduction band is highly reducing. At the outer surface, the excited hole and electron can proceed redox reaction with adsorbed species. The charges can directly act upon the adsorbed pollutants. Oxidation of OH^- by the hole generates the hydroxyl radical ($OH^\cdot$), a very powerful and indiscriminant oxidant. ($OH^\cdot$) attack at the surface of pollutants and possibly in solution as well and these are usually the very important radicals formed during TiO_2 photocatalysis. The conduction band electron is reducing the adsorbed O_2 to $O_2^\cdot$. It prevents the electron from reunion with the hole and results in an amassing of oxygen radical species that can also take part in attacking contaminants.

Main reactions governing the photocatalysis process are as follows (Turchi and Ollis, 1990):

$$\mathrm{TiO_2} + h\nu \rightarrow e^-_{cb} + h^+_{vb} \tag{6}$$

$$h^+_{vb} + \mathrm{H_2O} \rightarrow \mathrm{OH}^\cdot + \mathrm{H}^+ \tag{7}$$

$$h^+ + \mathrm{OH}^- \rightarrow \mathrm{OH}^\cdot \tag{8}$$

$$h^+ + R_{ads} \rightarrow R^+ \tag{9}$$

$$e^-_{cb} + \mathrm{O_2} \rightarrow \mathrm{O_2^{-\,\cdot}} \tag{10}$$

$$e^-_{cb} + h^+_{vb} \rightarrow \mathrm{Heat} \tag{11}$$

CHAPTER 3

LITERATURE REVIEW

3.1 Pharmaceuticals in natural water, surface water and waste water

Pharmaceutical being disposed off from hospitals, pharmaceutical industries or domestic waters is an issue of growing concern as they affect the natural environment (Gultekin and Ince 2007, Khetan and Collins, 2007,Oulton et al. 2010). Pharmaceuticals have been found in river water which was linked to removal of fish living downstream of wastewater treatment plant (WWTP) outfalls (Ternes et al. 1999). The overall impact of such discharges on flora and fauna is uncertain and the risks are still being accessed.

Sources of pharmaceuticals in the environment include municipal WWTPs, WWTPs of pharmaceutical production facilities, hospital effluent, and agricultural run-off, land spreading of sewage sludge, aquaculture and even landfills (Khetan and Collins 2007).

In the past decade, it has become possible and reliable to determine the concentration of PPCP in groundwater at trace level. The concentrations of pharmaceuticals are frequently detected in groundwater at trace level.

Antibiotics being extensively used for human and veterinary medicine are metabolized and unmetabolized secreted through feces and in urine have already been detected in wastewater treatment plants and surface water(Hirsch et al. 1999). The samples of surface water showed the appearance of erythromycin degradation products including roxithromycin and sulfamethoxazole. They are partially degraded in the environment and as a result are likely to accumulate in water bodies. Sulfonamides are mostly studied and have been found in high concentration. Possible emission sources for PPCP in groundwater, such as wastewater and contaminated surface water, landfills, septic systems, livestock breeding and sewer leakage (Sui et al. 2015).

One of the most cited examples of the dangers of pharmaceuticals in the environment is the effect of diclofenac, which is a non-steroidal anti-inflammatory drug (NSAID) on the populations of long-billed vulture (Gyps indicus), oriental white-backed vulture, (Gyps bengalensis) and slender-billed vulture (Gyps tenuirostris) on the Indian subcontinent.

(Markandya et al. 2008)In the period 1992–2007 the populations of the former two declined by 96.8 % and 99.9 % respectively and similar declines occurred in the slender-billed vulture (Gyps tenuirostris). A post-mortem examination on 259 adult and sub-adult oriental white-backed vultures was done and it was found that 85 % showed evidence of renal failure. Tests for diclofenac residue found concentrations of diclofenac (0.051 μg/g – 0.643 μg/g) in the 100 % of the vultures that died of renal failure, while no diclofenac was found in vultures that died from other causes (Taggart et al. 2007). The high concentrations triggered the renal failure in vultures that were orally administered diclofenac in a control study. Diclofenac was prescribed for veterinary use on livestock due to its analgesic, anti-inflammatory and antipyretic properties. The decline of the vulture populations is not just a loss for ecosystems.

3.2 Removal of pharmaceuticals from wastewater using conventional treatments

Pharmaceuticals used in veterinary and human medicine are released into surface waters without passing through a wastewater treatment plants, making their control and follow-up much more challenging. The ground could act as a major source of water contamination. Chlorine is still the most widely used conventional treatment for disinfecting of drinking waters (Rivera-Utrilla et al. 2013). Various studies on the chlorination of aromatic compounds showed that the Cl reaction rate could be strongly affected. Studies on the removal of acetaminophen, paracetamol, showed that it reacts with chlorine to form numerous subproducts, two of which have been identified as toxic compounds.

The conventional plants have a limited capacity to remove pharmaceutical products from urban wastewaters, as many of the compounds could not be metabolized by microorganisms as source of carbon and they might even hinder the activity of the microorganisms or bioaccumulation could be produced in the food chain (Ternes 1998) . Recent studies exhibit that conventional treatment plants based on the use of microorganisms, are inappropriate to efficiently destroy various type of compounds, due to low concentrations in the water and due to their complex structure (Halling-Sorensen et al. 1998).

In short, conventional treatment processes are not capable of completely efface large amount of the organic micropollutants which are present in urban wastewaters. More specific treatments and efficient treatments are required to reduce the environmental impact of effluents and adhere with increasingly strict legislation. Tertiary water treatments includes biological systems to remove nitrogen, chemical precipitation to remove phosphorus, ionic exchange to remove ions, distillation to remove volatile organic compounds, adsorption on activated carbon to remove organic and inorganic pollutants and liquid-liquid extraction.

The activated carbon has the capability to adsorb the pollutants. It is a function of both the concentration and characteristics of the pollutants and the temperature. Adsorption isotherm is used to determine the material adsorbed at constant temperature (Singh et al. 2011).The most common adsorption isotherm equations used in water and wastewater treatment are Freundlich isotherm and Langmuir isotherm (Dutta et al. 1999). Activated Carbon is mainly used for the treatment of pollutants within liquid phases as well as gaseous phases. The main advantage of using activated carbon to remove pharmaceuticals is that it does not generate toxic orPhACs. According to the literature, activated carbon generally shows a high capabiliity to adsorb pharmaceuticals.

The advantages of membrane processes are the high separation efficiency, the flexibility and the energy-efficient operation(Toth et al. 2011). During the operation scaling and fouling must be prevented. It is also important to emphasize that membrane process can separate materials that no other process could. It is also environmentally beneficial because no further waste is generated.

Micropollutants could also be removed by membrane filtration (reverse osmosis and nanofiltration) or adsorption on activated carbon but the retention capacity of both methods is reduced through blockage by natural organic matter present in water (Wei et al. 2010).

Literature on the release of APIs (Active pharmaceutical ingredients) into the environment is focused on APIs in effluent from municipal wastewater. APIs in this effluent are the main source of APIs in surface water. Primary treatment consists of screening stage where large debris and grit are removed. This step may also include fat oils and grease removal, pH adjustment, hydraulic flow equalization, temperature adjustment and an initial sedimentation stage depending on local plant conditions/requirements. The most common type of secondary wastewater treatment is activated sludge type processes. The wastewater flows to an aeration tank containing microorganisms that oxidise the wastewater. This suspension is then pumped to a settling tank where the microorganisms settle and are removed as sludge or re-circulated back into the aeration tank. The super latent from the settling tank is discharged or flows to a tertiary treatment step where nutrients and/or micro-pollutants are removed. At this stage AOPs could be used to remove APIs.

A critical review of API removal by different water treatment technologies was done by by Oulton et al. (2010). The analysis included plants that used conventional activated sludge and other unconventional designs; membrane bioreactors (MBRs), sand filtration, ultra-, micro-, and nano-filtration, reverse osmosis, activated carbon, and chemical oxidation via ozonation for water treatment. Treatment efficiencies varied for APIs, for example, in conventional treatment ibuprofen was removed by greater than 1-log10 (90 %); in contrast antiepileptic carbamazepine is barely removed as influent and effluent concentrations are almost identical. Removal efficiency also varies between technologies. Conventional activated sludge demonstrated an average removal rate of 61 % for all APIs. Proponents of MBR technology claim it offers significant improvement compared to activated sludge with an average API removal rate of 86 %. However these results vary significantly between studies and range of values of these systems is the same as activated sludge (Verlicchi et al.2012). Even if MBR does not remove more APIs, they possess other advantages such as higher solids removal and high solid retention times (SRT) within compact reactor volumes which improves pollutant removal (Clara et al. 2005).

Technologies intended as a tertiary “polishing” step after primary and secondary treatments were also reviewed by Oulton et al. (2010). Ozonation is effective for API removal in a wastewater matrix and can degrade species such as carbamazepine which are recalcitrant to conventional biological degradation. The results surveyed were from a test facility treating high total organic carbon (TOC) wastewater. AC was successful at removing APIs in this matrix but performance hinged on the use of fresh AC with frequent regeneration. Removal by membrane technologies varied depending on membrane type. Microfiltration membranes outperformed ultrafiltration membranes, while nanofiltration and reverse osmosis performed the best with average removal rates >98 %. The issue of membrane fouling and the treatment of concentrates (the rejected water containing a higher concentration of pollutants and minerals) were not investigated. In contrast, ultrafiltration was found to have low effectiveness as studies using it removed on average >15 % of the APIs in the influent as the pores of these membranes are too large to exclude APIs. The results showing that microfiltration is better than ultrafiltration appear contradictory; however, this is like due to the low number of studies for these technologies.

The conventional processes are occasionally not capable of removal of pollutants to the levels required by law or are essential for the subsequent use of the effluent. Activated sludge process produces large amount of sludge which is difficult to handle. Hence, AOPs are suggested for the treatment as they are effective in the treatment of organic as well as inorganic compounds.

3.3 Removal of pharmaceuticals from wastewater using AOPs

AOPs are the processes that involve generation of highly reactive species such as the $OH^{\bullet}$, which is the most robust oxidizing component after fluorine having an oxidation potential of 2.80V (Parsons and Williams, 2004). $OH^{\bullet}$ is non-selective unlike many other radicals, and thus it readily attacks a large group of organic compounds and converts them to products which are less complex and less harmful intermediate. At proper operation conditions and sufficient contact time, it is practically possible to mineralize the target pollutant to CO_2, which is the most stable and desirable end product of chemical oxidation. The remarkable advantage of AOPs over all biological and chemical processes is that large amounts of hazardous sludge is not produced as in case of activated sludge process and end products are non toxic.

A critical review of pharmaceutical removal by different water treatment technologies is analysed over many published studies on different pilot- and full-scale WWTPs or treatment configurations by Rivera-Utrilla et al.(2013). Most of the research is focused on the application of O_3/H_2O_2, O3, O_3/ OH^- and O_3/activated carbon systems for the removal of pharmaceuticals from water. In some cases, the removal efficiencies obtained from direct ozonation were low and they increased up to 100% when the ozonation was carried out in the presence of H_2O_2 or activated carbon (Rivera-Utrilla et al. 2013) .Most pharmaceuticals are photoactive as they use luminous radiation for absorption. Various studies have shown that numerous PhACs can be degraded, as they generally contain heteroatoms, aromatic rings and other functional groups that absorb solar radiation and produce reactions with photosensitizing species that induce their photodegradation in natural water. The percentage removal obtained by using UV radiation alone were quite low (lower than 30%), and they reached values around 100% when adding TiO_2, H_2O_2, or TiO_2/activated carbon. Very less research has been reported on the use of γ-radiation to remove pharmaceuticals from wastewater. The proven adequacy of this technology to remove the pollutants from wastewater efficiently has prompted research interest in its usefulness for the removal of pharmaceutical products. The pharmaceuticals percentage removal values reported were higher than 50%, and, in most cases, these values are very high. High percentage removal are accompanied by a reduction in both TOC and solution toxicity.

Many electrochemical processes are available for the removal of wastewater which is contaminated by organic pollutants such as pharmaceutical micropollutants, whose presence in the environment has lead to a major concern.

Medical substances have been detected in sediment samples originating from antibiotics in feed additives and in ground water samples originating from spills(Halling-Sorensen et al. 1998). A study showed that quite a number of high volume substances were found to exist in the sewage treatment plant. Regular therapeutic use might be the cause of a substance carried by sewage effluent into the aquatic system, ground and tap water samples.

Gomez-Pacheco et al. (2011) investigated the effectiveness of technologies based on the simultaneous use of O_3– H_2O_2, O_3-biological process and O_3-AC in the removal of tetracyclines from water. The results obtained showed that tetracyclines degradation was completed after 10 min of ozonation. Total organic carbon and toxicity removal was observed with longer ozonation.

Mohapatra et al.(2014) studied that due to the higher consumption of carbamazepine most of oral carbamazepine dose is excreted unchanged in urine and feces. Several AOTs have been developed and optimized in recent years for wastewater treatment, in order to obtain better precision. Different extraction method such as GC–MS/MS, HPLC, LC–MS, GC–MS, or LC–MS–MS. Carbamazepine has proved ineffective as its removal in watewater in most cases is causing the way for the installation of different treatment methods; hence AOPs for its complete removal from wastewater are used.

Babu et al. (2009) examined the electrooxidation for analysis of pharmaceutical wastewater. The wastewater contained mainly gentamicin and dexamethasone. NaCl was used as supporting electrolyte. The effluent was treated in a reactor which was in continuous (single pass) mode and cylindrical under various current densities and flow rates. The efficiency of COD reduction and power consumption were studied for different operating conditions. FT-IR spectrum were also studied which showed that during electrooxidation, the intensities of functional groups such as N-H, O-H were reduced and some new peaks also started to appear. The experimental results showed that electrooxidation treatment was very efficient and capable of elevating the quality of treated wastewater.

Electrooxidation using BDD(boron doped diamond electrodes) has properties that make them suitable for a use in wide variety of operations (Barrios et al. 2015). Electrooxidation was applied to sludge from a treatment plant which was obtaining discharge from industry located in Toluca, Mexico. Different operating parameters were tested based on (sCOD) reduction. Oxidation of organic compounds was hindered by the concentration of solids during treatment as phased separation flotation occurred due to gas generation and additional tests were performed to overcome this situation.

The Fenton process has been studied for wastewater treatment. The process consists of the generation of hydroxyl radicals ($OH^{\bullet}$) by the reaction between ferrous ions and H_2O_2 (Fenton's reagent).The additional $OH^{\bullet}$ can degrade organic contaminants. Fe^{2+} absorbs light > 400nm at low pH (2 - 4) and therefore allows a great proportion of the solar spectrum to be used (Malato et al. 2002). Fenton reactions operate at room temperature and normal pressure. Intricate apparatus are not required for its use.

Manu & Mahamood (2012) reported that NAID (non-steroidal anti-inflammatory drug) are extensively used. Several adverse effects have been reported due to presence of Diclofenac in the wastewater and hence it should be removed from the environment. Fenton oxidation is found to be an effective classic process for the removal of organic contaminants. At the optimum conditions 74.25 % diclofenac reduction and 72.80 % of COD removal are observed in 240 minutes reaction time. The kkinetics fowed was pseudo second order. The

Fenton oxidation process proved to be the most effective in degradation of Diclofenac in water.

15 emerging contaminants (ECs) at low concentration in real effluent of municipal wastewater was detected and the treatment lead to degradation with the help of photo-Fenton in a pilot-scale solar reactor (Klamerth et al. 2010). The degradation of 15 compounds (Caffeine,Acetaminophen, Ketorolac, Atrazine ,Antipyrine, Carbamazepine, Flumequine, Hydroxybiphenyl, Ibuprofen, Isoproturon, Diclofenac, Ofloxacin, Sulfamethoxazole , Progesterone and Triclosan), each with an initial concentration of 100 µg L^{-1} and on the type of water (simulated water, simulated effluent wastewater and real effluent wastewater), but is relatively independent of the type of acid used for release of hydroxyl radicals scavengers, pH

and the initial hydrogen peroxide concentration used. Toxicity tests with Vibrio fisheri was conducted for the degradation of the compounds in real effluent wastewater which showed increase in toxicity.

Beta blockers including Atenolol and metoprolol are used as cardiovascular pharmaceuticals (Veloutsou et al. 2014) .It has been interpreted that with increase in H_2O_2 concentrations and of iron concentrations increases the degradation of atenol and metoprolol. The kinetics followed for the degradation was pseudo-first order. In general the photo-Fenton method has proved to be effective in mineralizing and decomposing and the compounds effectively.The by-products generated during the degradation was found using LC-MS/MS equipment and the toxicity of the treated solution was evaluated at different stages of the process.

3.3.1 Photodegradation and photocatalytic degradation

In the past few years, the photocatalytic and photolytic degradation of antibiotics was studied using different light sources including UV light, solar simulation and natural sunlight for a variety of water. Most pharmaceuticals absorb luminous radiation. Various studies have demonstrated that numerous PhACs can be photodegraded, since they generally contain aromatic rings, hetero atoms, and other functional groups. Table 3.2 shows the literature surveyed on photocatalytic and photolytic treatment.

Photocatalytic degradation of ECs (emerging contaminants) from waste water treatment plant and biological secondary treatment effluents was studied.The reaction rate is limited due to the weak absorption of photons at the low concentration of the catalyst in current reactor designs, under natural sunlight when CPC reactors of larger diameters are used a higher extent of emerging contaminants degradation was possible (Prieto-Rodriguez et al. 2012).The use of low concentrations of TiO_2 could be a economical, good, and simple alternative for the tertiary treatment of wastewater treatment plants and for the removal of persistent ECs which are not degraded by traditional waste water treatment plants. An approach for increasing the absorption of solar radiation involves the use of tubular reactors and compound parabolic collector (CPC) with a wider tube diameter to allow optimal absorption of photons.

The sonolytic, photocatalytic and sonophotocatalytic degradations of ibuprufen with the help of of Fe^{3+} and TiO_2 were studied (Madhavan et al. 2010). A higher degradation was observed for sonophotocatalysis in the presence of TiO_2 or Fe^{3+}. Even though TiO_2 sonophotocatalysis showed an additive process effect in the complete removal and mineralization a significant synergy effect was observed for the sonophotocatalysis in the presence of Fe^{3+}. This might be due to the formation of photoactive complexes between Fe^{3+} and IBP degradation products, such as carboxylic acids. HPLC and ESMS techniques were used for the identification of the intermediates which were formed by degradation. The sonication of IBP led to the formation of its mono- and di-hydroxylated intermediates.

Kaur et al. (2016) studied a critical evaluation on the treatment of NSAIDs using TiO_2 as a photocatalyst. TiO_2 photocatalysis is a valuable process for the removal of NSAIDs from wastewater. Reaction kinetics and optimization of the operational parameters such as TiO_2 loading, pH and initial drug concentration were studied. Less amount of work is published on the identification of intermediates formed during the degradation reaction. Very less work on the photocatalytic degradation of pharmaceutical drugs using visible and solar light active photocatalyst has been done so far. Therefore, to improve the solar efficacy of wide band gap semiconductors under solar irradiation, to facilitate visible light absorption modified nanomaterial should be used.

Chatzitakis et al. (2008) investigated the photocatalytic degradation of antibiotic drug Chloramphenicol, in solution using semiconductors as photocatalysts. Pseudo-first-order kinetics was followed by the degradation of compound .It could be seen that, with TiO_2 as photocatalyst and illumination quantitative degradation of the organic compound occured. The dechlorination of the substrate was complete at that time, while the organic N was recovered in the form of NO_3^- and NH_4^+ ions. The effect of temperature on the degradation rate of Chloramphenicol showed similar apparent activation energies for both ZnO and TiO_2 as photocatalysts. While the Kirby–Bauer method showed a 100% reduction of the drug activity after 90 min of photocatalytic treatment.

Chen and chau (2015) investigated the treatment of norfloxacin using Bi_2WO_6 as a photocataly. The efficiency of photocatalysis, photolysis, photocatalysis-via direct hole oxidation and $OH^\bullet$ was 79.3, 5.7 and 15% respectively. The $O_2^{\bullet-}$ radicals mainly act as an electron carrier to reduce the electron-hole recombination. The role of $OH^\bullet$ and h^+ was further confirmed by the effect of inorganic ions of SO_4^-, HCO_3^-, Fe_3^+ and Fe_2^+. There were three decay pathways for drug: decarboxylation, defluorination,piperazine ring transformation. A mathematical model was developed and the major intermediates were predicted in the process.

Salma et al. (2016) showed the effect of pH on both degradation mechanism and reaction kinetics of ciprofloxacin for UV photolysis and photocatalysis (TiO_2/UV-C). It could be seen that the removal rates strongly depended on pH.

Sulfamethoxazole's photochemical transformation was studied by Trovo et al. (2009) in seawater (SW), distilled water + NO_3^- (10 and 20 mg l^{-1}) and distilled water (DW) to examine the toxicity its persistence, and degradation pathway. Transformation products were identified which were performed in distilled water by liquid chromatography- time of flight-mass spectrometry of irradiated. To find out acute toxicity in distilled water Vibrio fischeri and Daphnia magna bioassays were used. Differences in the degradation rates were observed between distilled water and sea water,and was slower in sea water. Nitrates were present in distilled water which did not affect sulfamethoxazole degradation rate. Analysis by LC–TOF–MS was done and 9 transformation products during photolysis in distilled water were identified. Only 3 of previously reported were detected. The photo isomerization and rearrangement of the isoxazole ring cleavage of the sulfonamide bond represent the main pathways, at the time that generate the most abundant and persistent intermediates. The toxicity test was conducted of sulfamethoxazole solution and it showed different results according to organisms tested. Most sensitive of all the organisms was Daphnia magna which showed an increase in immobilization fromsixty to hundred percent after the irreadiation of thirty hours.

3.3.1.1 Antibiotic model compound: ornidazole

Nitroimidazoles are antibiotic and drugs against protozoal infectionsthat are mostly used in human medicine and veterinary treatments. Nitroimidazoles and their metabolites are supposed to possess carcinogenic and effect genotype hence, they are banned in EU (European Union). Trace amounts of Nitroimidazoles in edible animal tissues has been of great concern over the past few decades. There is a requirement to generate reliable and sensitive methods to study the remains of these compounds in different matrices. There are other pharmaceutical compounds which have become important environmental pollutant which have been detected in groundwater, drinking water, wastewater-treatment effluents, receiving waters. Mainly environmental matrices and biological are mostly studied. The elaborated explanations of areas, including sample treatment and detection systems focuses on the problems of confirming analytes at low levels of concentration.

Ornidazole has its chemical representation as 1-chloro-3-(2-methyl-5- nitroimidazole-1-yl) propan-2-ol, is an antibiotic, which is mostly used in both veterinary medicine and human medicines. It has been detected in ground water, surface water, wastewater and drinking water, as well as in river bed sediment and in soil. Its continuous flow into environment may lead to accumulation and low level environmental exposure which results in negative effects on ecosystems and on life and as studied by Sams.et al (1998). Ornidazole must be completely eradicated from the environment due to its properties. So far, ornidazole‘s photolytic stabilityhas been reported in aqueous solution (Govaert et al. 2000). However degradation of ornidazole using different AOPs has not been studied. Detailed mechanistic study was shown using photocatalytic degradation. The proposed mechanism showed a number of intermediates and showed different pathways involved as shown in Fig 3.1.

Zhao et al. (2012) inspected the ornidazole's degradation using Y^{3+}- $Bi_5Nb_3O_{15}$ as a catalyst and the feasibility was explored of using Y^{3+}- $Bi_5Nb_3O_{15}$ to treat antibiotics in wastewater as shown in Table 3.2. From the results it was concluded that the Y^{3+}- $Bi_5Nb_3O_{15}$ exhibited single-crystalline orthorhombic structure having small particle size (20–100 nm); It was found that the UV–vis absorbance edges significantly shifted to the visible-light region.The nanoparticles showed high photo-catalytic activity in the degradation of ornidazole and different possible pathways of degradation of ornidazole were proposed according to the results of spectrometry UPLC-MS.

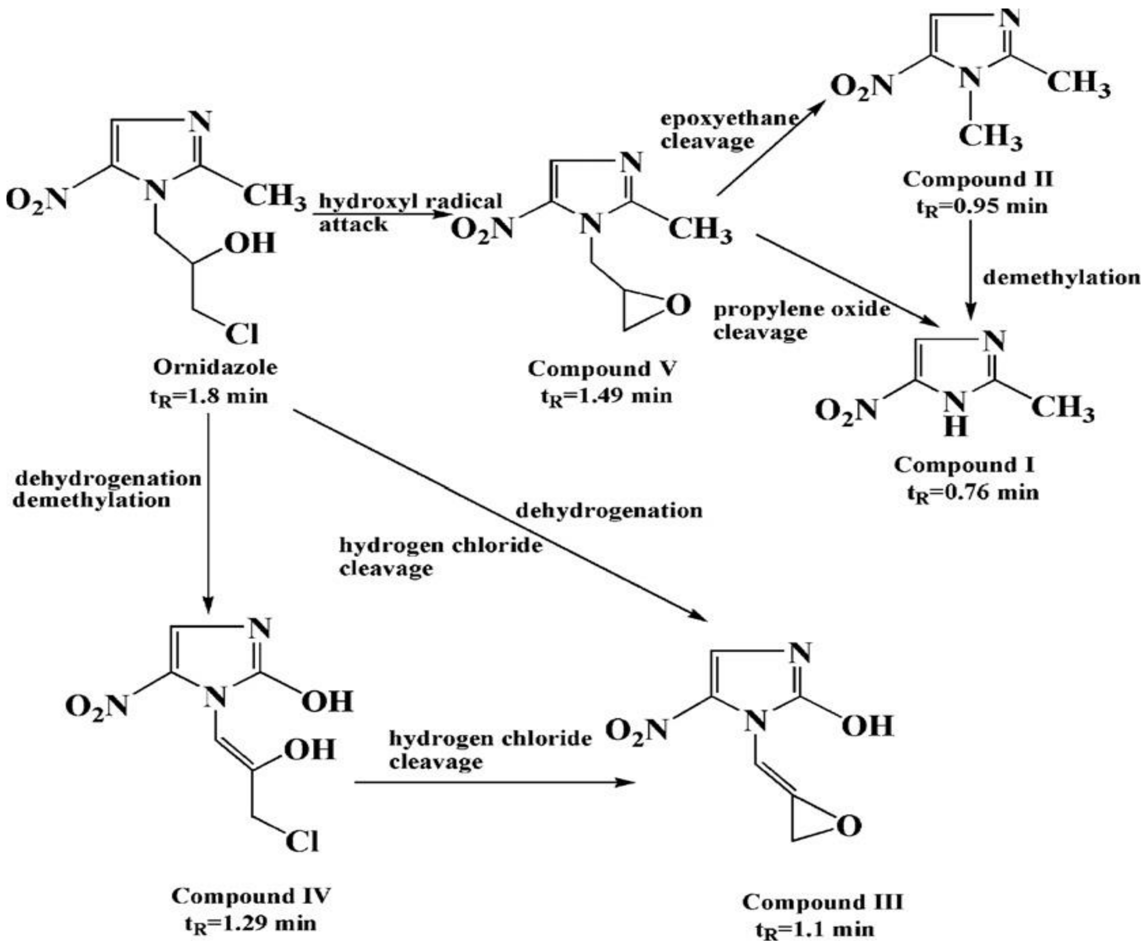


Fig3.1: Proposed pathway of degradation of ornidazole by photodegradation (Zhao et al. 2012)

Table 3.2: Literature reviewed for photocatalytic degradation of pharmaceutical compounds

Therapeutic class/compound	Treatment	Water matrix	Experimental conditions	Results	Reference
			Antibiotics		
sulfamethoxazole, roxithromycin, erythromycin, ciprofloxacin, sulfathiazole	DP	MQ water, Fresh water & salt water	16-mercury vapor lamps (UV 254 nm) or black light phosphor bulbs (UV 350 nm).	The photolysis of sulphamethoxazole showed complete degradation within 1 min	Batchu et al. (2014)
Moxifloxacin	PC	Deionized water	UV-A lamp (λ_{max} = 365 nm)	Maximum degradation rate of moxifloxacin was achieved by using air sparging and 5 gl^{-1} TiO_2.	Van Doorslaer et al.(2012)
Ornidazole	PC	Milli-Q water	visible light source 500 W halogen tungsten lamp (500W)	Degradation efficiency of Y^{3+} -$Bi_5Nb_3O_{15}$ and $Bi_5Nb_3O_{15}$ reached 90.5% and 80.3%. COD values decreased with increasing illumination time from an initial value.	Zhao et al. (2012)
Amoxicillin (ampicillin and cloxacillin)	PC	DW	UV lamp (6 W,365 nm)	At lower pH with addition of H_2O_2 and TiO_2 dose of 0.1 gl^{-1} led to complete degradation of all antibiotics.	Elmolla & Chaudhuri (2010)
Paracetamol	DP and PC	MQ water	UV-C (15 W)& Black light blue UV-A (8 W)	Rapid degradation of paracetamol and complete mineralization in the presence of TiO_2 under UV-C irradiation.	Yang et al. (2008)
Ibuprofen and Ketoprofen	DP	MQ water	UV (254 nm) and UV/V-UV (254/185 nm)	V-UV irradiation enhanced the degradation rate of ibuprofen while degradation rate of ketoprofen was much higher (40 times) under UV irradiation.	Szabo et al. (2011)

Ketoprofen &diclofenac	DP	Ultrapure water and secondary effluents	Low pressure Hg lamp (254 nm) Medium pressure Hg lamp (150 W; 200-450 nm)	Ketoprofen displayed the highest time and fluence-based rate constants followed by atenolol &diclofenac under medium pressure Hg lamp irradiation	Salgado et al. (2013)
Anticonvulsants					
Carbamazepine (Clofibric acid, iomeprol,	PC	MQ water	Solar simulator Xe short arc lamp (1000 W)	Degradation of carbamazepine was faster by using TiO_2 as a catalyst due to higher adsorption.	Doll & Frimmel (2005)
Carbamazepine and ibuprofen	PC	wastewater from WWTP& MQ water	Solar simulator (1000 W) Phillip Xe lamp) and UV-A lamp (9 W Radium lamp)	Degradation under UV irradiation in milli-Q water was sensitive to TiO_2 catalyst loading. Solar and UV-A photocatalysis appeared to be effective for carbamazepine degradation.	Achilleos et al. (2010)
Clofibric acid & Lipid regulators	DP	MQ water and secondary effluent from WWTP	Low pressure Hg lamp (10 W; 254 nm)	Temperature greatly influenced the degradation rate of clofibric acid in filtered wastewater. Photolysis rate, however, decreased compared to in Milli-Q water under investigated temperatures. Humic acid showed negative effect on the degradation.	Li et al. (2010)
Metoprolol Beta-blockers & propranolol	PC	MQ water	Solar simulator (Xe-OP lamp; 1 kW)	Maximum removal of both compounds was achieved with $0.4\ gl^{-1}$ TiO_2 P25. Almost 55% of TOC and COD removal was achieved after	Romero et al. (2011)

*PC-PhotoCatalytic

**DP-DirectPhotolysis

RESEARCH GAPS

Based on the literature review the following research gaps have been identified:

1. There was no literature available on the photocatalytic degradation of ornidazole in presence of UV light.
2. No study was reported for the photocatalytic degradation of Ornidazole using immobilized photocatalyst.
3. Very less work has been reported for the photocatalytic treatment of real pharmaceutical wastewater.

OBJECTIVES

Based on the critical literature review, the following objectives have been set for the present work:

1. Photocatalytic degradation of the model compound Ornidazole, in presence of suspended TiO_2 semiconductor and UV light in slurry pond reactor.
2. To carry out parametric studies for Photocatalytic degradation of the Ornidazole.
3. To study the photocatalytic degradation of Ornidazole using immobilized TiO_2 photocatalyst.
4. Photocatalytic degradation of the real pharmaceutical wastewater, in presence of suspended TiO_2 semiconductor and UV light in slurry pond reactor.
5. To study the effect of process parameters such as pH, catalyst dose, and time (t) on photocatalytic degradation of the real pharmaceutical wastewater.

CHAPTER 4

MATERIALS AND METHOD

This chapter portrays the materials used and methods adopted for carrying out the photocatalytic degradation of the pharmaceutical wastewater. In materials section, properties and specifications of the materials used has been depicted in detail. In equipment and instruments part, all the details of the instruments used to carry out the experiment like its specifications and application have been described in detail. In the last section i.e. methodologies, the procedures to carry out the various experiments have been given.

4.1 Materials

4.1.1 Pharmaceutical drug

a) **Ornidazole** having chemical representation as 1-chloro-3(2-methyl-5-nitroimidazole-1yl) propan-2-ol is well known antibiotic and antiparasitic drug is commonly used for the treatment of anaerobic infections, amoebiasis, giardiasis and trichomoniasis and it is mostly prescribed for use in abdominal and gynaecological surgery. Ornidazole has been identified in ground water, wastewater, surface water, drinking water and also in river bed sedimentand in soils (Eurin et al. 2011). Its continuous augmentation in water leads to negative effects on ecosystem hence it has to be completely eliminated from environment. There is no much information available on degradation of ornidazole by AOPs.

b) **Real pharmaceutical wastewater** was collected from a pharmaceutical industry in Himachal Pradesh, India.

4.1.2 Catalysts used

AEROXIDE TiO_2 P25 was obtained from Evonik Degussa Corporation, USA. Its physico-chemical data is given in Table 4.1:

Table 4.1: Physico-chemical data of TiO_2 P25

Properties	Units	Typical Value
Appearance		Fluffy White Powder
Specific surface area (BET)	m^2/g	50±15
Average Particle size	Nm	30
Behaviour towards H_20		Hydrophilic
Crystalline polymorphs		70% anatase and 30% rutile
Tamped Density	g/l	130
pH in 4% dispersion		3.5-4.5
Titanium Dioxide Content	wt%	≥ 99.5
HCl Content	wt%	≤ 0.3
Al_2O_3 Content	wt%	≤ 0.3
Fe_2O_3 Content	wt%	≤ 0.01
SiO_2 Content	wt%	≤ 0.2
Application		Photocatalytic reaction, raw material, adsorption and thermal stability

4.1.3 Reagents and chemicals

Hydrochloric acid and sodium hydroxide were bought from S. D. Fine Chemicals Limited, India were used to adjust the pH. For all the performed experiments, distilled water(DW) was used.

4.2 Equipment and instruments

4.2.1 pH meter

The pH of the pharmaceutical drug samples was changed by adding NaOH or HCl solution as per requirement and was measured by using Thermo Scientific Orion Star Series pH Meter.

4.2.2 Magnetic stirrer

A magnetic stirrer or magnetic mixer is a device that exploits a rotating magnetic field to cause a magnet bead which is immersed in liquid to spin very rapidly, thus stirring it. The rotating field is created either by a set of stationary electromagnets or rotating magnet, placed underneath the vessel with the liquid. Magnetic stirrers might have a hot plate or some other means for heating the liquid. Spinit Magnetic Stirrer was used for the experiments.

4.2.3 Centrifugation (filtration)

After the photocatalytic treatment of the pharmaceutical drug sample, the suspended TiO_2 particles are needed to be separated from the pharmaceutical drug sample before measuring its absorbance. The TiO_2 particles were separated by using Hitachi High Speed Micro Centrifuge CF15RXII. A centrifuge is an instrument which spins liquid samples at high speed (15,000 rpm) with the help of motor. The centrifuge works using the sedimentation principle, where to separate substances of greater and lesser density centripetal acceleration is used.

4.2.4 UV-VIS spectrophotometer

For determining the concentration of various compounds, we first measured the absorbance of the pharmaceutical drug sample at λ_{max} using UV-Vis spectrophotometer. Then we use calibration curve (concentration versus absorption curve) to determine the concentration of the pharmaceutical drug sample. The concentration of the pharmaceutical drug was indirectly determined by measuring absorbance. For measuring absorbance of the pharmaceutical drug samples, Perkin Elmer Lambda 35 UV-Vis spectrophotometer was used.

4.2.5 UV chamber and shallow pond reactor

A lab scale set up for shallow pond reactor is shown in Fig.4.1. The photocatalytic degradation studies were conducted using shallow pond slurry reactor. For conducting experiments a batch type bench scale photocatalytic reactor system was fabricated. The set up consisted of a batch reactor placed on a scaffold under UV light. A borosil glass vessel of 500 ml capacity was used as the shallow pond reactor and UV rays were irradiated on the glass vessel. This reactor is placed on a magnetic stirrer for complete mixing of contents, so that the TiO_2 remains suspended and the concentration of the pollutant within the reactor could be assumed to be constant at any time. Fig 4.2 shows the schematic diagram of slurry mode reactor.

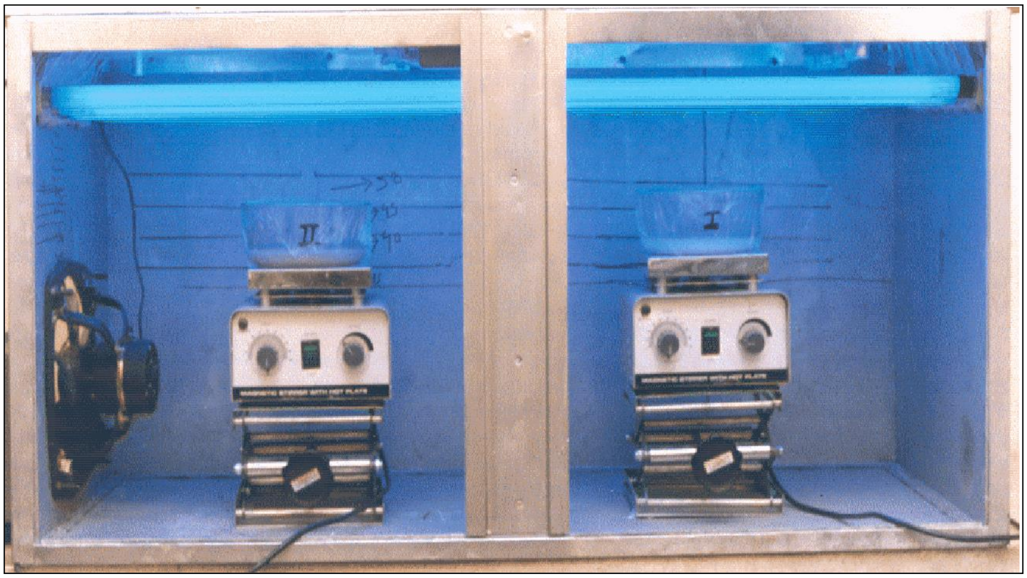
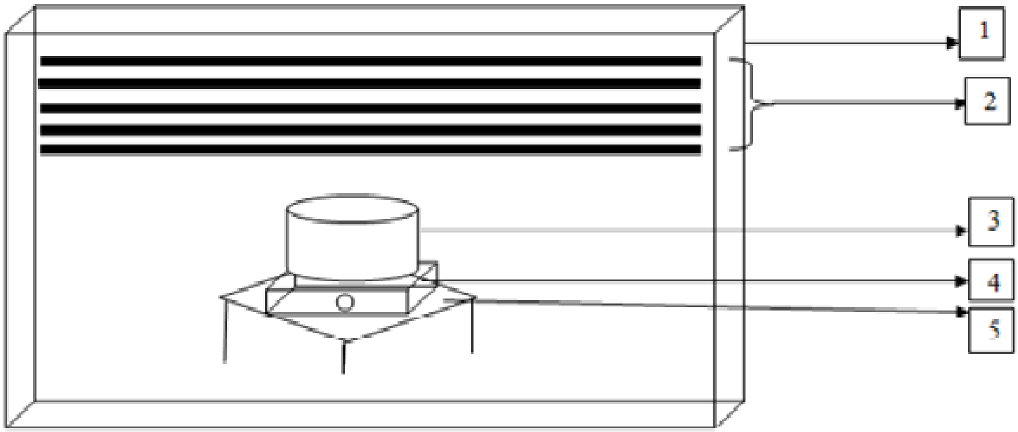


Fig 4.1: Experimental Setup consisting of UV chamber, magnetic stirrer and slurry pond reactor



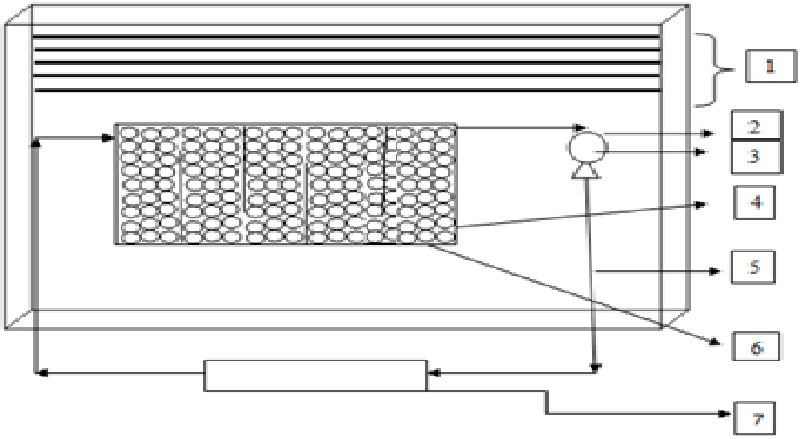
(1) UV Chamber (2) UV Light (3) Glass reactor (4) Magnetic stirrer (5) Stand

Fig 4.2: Schematic diagram of slurry reactor

4.2.6 Fixed bed reactor

A schematic representation of lab scale set up for fixed bed reactor having dimensions (25cm×30cm×5cm) (length ×breadth ×height) as shown in Fig 4.3. The photocatalytic degradation studies were conducted using fixed bed reactor. Fig 4.4 shows the schematic diagram of fixed mode reactor. The solution containing the wastewater of known concentration was transferred into the reactor with the help of pump. The flow rate was adjusted to 500ml/hr. A batch type photocatalytic reactor was fabricated for conducting experiments. The set up contained a reactor which is placed on a scaffold under UV light. The cement beads immobilized with TiO_2 were put inside and the reaction was started.

Fig 4.3: Experimental Setup consisting of UV chamber and fixed bed reactor



(1)UV Source (2)UV Chamber (3)Perisphaltic Pump (4) Coated cement beads (5) Recirculation (6) Fixed bed baffled reactor (7) Container for storage

Fig 4.4: Schematic diagram of fixed bed reactor

4.3 Experimental procedure

4.3.1 Procedure for photocatalytic experiments using shallow pond slurry reactor under UV light (for ornidazole)

The general procedure for all the photocatalysis experiments is as follow:

1. The stock ornidazole solution of concentration 500 mg L^{-1} (500 ppm) was prepared in distilled water (DW) for all the experiments.
2. Take desired ml of pharmaceutical solution from the stock solution in the shallow pond reactor.
3. In the shallow pond reactor, add the desired amount of the TiO_2 catalyst.
4. Then check the pH of the solution using Thermo Scientific Orion Star Series Meter.
5. The reactor is placed on the magnetic stirrer and magnetic bead is put in the solution for proper stirring.
6. UV lights are switched on. The door of the UV chamber is closed so that no UV rays come out and affect us.
7. After every 30 minutes, take 5ml sample from the reactor with the help of micropipette.
8. The photocatalysis is done for next 180 minutes.
9. To filter the suspended TiO_2 particles from the pharmaceutical drug sample, centrifugation is done using Hitachi High Speed Micro Centrifuge CF15RXII. Make sure the level of sample in each centrifuge tube is same**.** The centrifuge tubes are spun at the high speed of 15,000 rpm for 15 minutes. The TiO_2 particles get stuck to the walls of the tube.
10. A computer based UV-Vis spectrophotometer was used for determination of concentration of samples as per following:
    a) The system is switched on and warmed up.
    b) Thoroughly cleaned quartz cuvettes are taken.
    c) Both cuvettes are filled with distilled water and absorbance at λ_{max} (of drug) is checked. Auto zero is done.
    d)After auto zeroing, one cuvette is filled with the reference compound (distilled water) and the other one with the compound whose absorbance has to be measured at λ_{max}.
    e) To get the relationship between concentration and absorbance of the compound, a calibration curve is made. Calibration solutions are made from standard solutions of

known concentration. The absorbance is plotted against known concentration of the calibration samples. These calibration curves are stored in the system itself and the concentration of the unknown sample can be calculated directly from the absorbance.

11. Now, we know variation of concentration of compound with time. It decreases with time.

For degradation of compound with the above mentioned setup, the various experiments were conducted for optimizing the parameters like initial concentration, pH and catalyst loading.

4.3.2 Procedure for photocatalytic experiments using shallow pond slurry reactor under UV light (for real wastewater)

The general procedure for all the photocatalysis experiments is as follow:

1. Take desired ml of pharmaceutical solution from the stock solution in the shallow pond reactor.
2. In the shallow pond reactor, add the desired amount of the TiO_2 catalyst.
3. Then check the pH of the solution using Thermo Scientific Orion Star Series Meter.
4. The reactor is placed on the magnetic stirrer and magnetic bead is put in the solution for proper stirring.
5. UV lights are switched on. The door of the UV chamber is closed so that no UV rays come out and affect us.
6. After every 30 minutes, take 5ml sample from the reactor with the help of micropipette.
7. The photocatalysis is done for next 480 minutes.
8. To filter the suspended TiO_2 particles from the pharmaceutical drug sample, microfilters were used.
9. Then for the analysis COD was measured as following.
    a) 3ml of sample is taken in the COD vials.
    b) 1.5ml of $K_2Cr_2O_7$ is added to all the vials.
    c) 3.5ml of H_2SO_4 and Ag_2SO_4 solution is added slowly.
    d) Now the solution prepared is digested in COD digester for 2hrs at 150 ^{0}C.
    e) After digestions COD is measured.

4.3.3 Procedure for immobilization

The general procedure for immobilization is as follow:

1. 10 gm of TiO_2 was dissolved in 1*l* of distilled water with continuous stirring followed by sonication, until TiO_2 dispersed properly.
2. Immobilization of TiO_2 was done on cement beads (1-1.5 cm in dia). Cement beads were

made manually by using Portland cement and sand which were brought from local market.

3. The cement beads were coated with TiO_2 slurry and allowed to dry in oven at 100^0C.
4. Dry cement beads were calcined for 2 hr at 400 ^{0}C.
5. It was repeated for 3 times to get uniform coating of TiO_2 on the cement beads.

4.4 Modeling and optimization

Photocatalytic treatment of pharmaceuticals wastewater is, in general, quite complicated. This is caused by the complexicity of solving the equations that involve the radiant energy balance, mass transfer, the mechanisms of a photocatalytic degradation involving radical species and the spatial distribution of the absorbed radiation. Since the photocatalytic treatment of wastewater depends on numerous factors and the modeling of the photocatalytic treatment processes includes a multivariate system, it is obvious that this multivariate system could not be solved by simple linear multivariate correlation (Aleboyeh et al. 2005). It is also essential to study the interaction of parameters at a time.

Data collected from the experiments have been used for the ANN modeling and optimization was done by Response Surface Methodology (RSM) using the simulated data from ANN model.

Modeling by Artificial Neural Network

Artificial Neural Network (ANN) is an assuring modeling technique for photocatalytic degradation of data sets which have the non-linear relationships, which are mostly encountered in photocatalytic degradation of pharmaceutical wastewater. ANNs are simulated by biological neural systems. Neurons are the basic component of ANN (Kaur et al. 2015).Two types of ANNs are mostly used as multilayered feed forward neural network, which is trained by back-propagation algorithm and Kohonen self-organizing mapping (Agatonovic-Kustrin and Beresford 2000) . Back-propagation algorithm in ANN was used for learning the appropriate weights. The input layer act as receiver and shows the number of input variables used and output layer provide the response which shows the number of result variables whose value is to be predicted. The hidden layers act as feature detectors layers which are employed to perform nonlinear transformations on the input space and are mostly used for computation purposes (Bhatti et al., 2011). More than one hidden layer could be present. According to the theory of universal approximation a network having a single hidden layer and amply large number of neurons could be used to interpret any structure of input and output.

All ANN calculations have been carried out using Matlab 7.6 mathematical software with ANN toolbox.

Optimization by Box-Behnken Design (BBD)

To optimize the process parameters Box-Behnken designs (BBD) under response Surface Methodology (RSM) was used (Pareek et al. 2002). The output (response) Yi are the functions of inputs X_1, X_2, X_i,..X_f, which are obtained from the following relationship:

$$Y_i = \Phi(X_1, X_2, X_3... Xi ...Xf) \qquad (12)$$

The relationship between the input factors and responses are expressed as quadratic response model. The non-linear regression analysis was used to identify relevant model to fit the responses according to simulated results and input factors. In general, the model being used is best fitted in second-order polynomial equation.

$$Y = s_0 + \sum_{i=1}^{k} s_i X_i + \sum^{k} s_{ii} X_i^2 + \sum\sum_{i<j} s_{ij} X_i X_j + \kappa_t \qquad (13)$$

Where, Y is response; s_0, s_i, s_{ii} , s_{ij} are constant coefficients and X_i the uncoded independent variables. Coding followed the three level factor, and coded as -1 (low) and +1 (high). To design the experiments, the Statistical Design-Expert software version 6.06 (STAT-EASE Inc., Minneapolis, US) was used.

CHAPTER 5

RESULTS AND DISCUSSIONS

This chapter consists of two sections; in first section we have studied the effect of operating parameters on the % degradation of pharmaceutical compound ornidazole by the photocatalysis process. In the second section real pharmaceutical effluent was treated using photocatalysis. The experimental results and their interpretation regarding pharmaceutical compound Ornidazole and real pharmaceutical wastewater degradation using photocatalysis have been discussed in detail. Photocatalytic treatment process has shown significant compound degradation.

5.1For synthetic waste model compound: Ornidazole

5.1.1 Calibration Curve

The complete wavelength scan of compound ornidazole was done on UV-Vis spectrophotometer and maximum absorbance was observed at 319nm. Standard curve as shown in Fig 5.1 was made to assess the concentration of compound ornidazole after photocatalytic degradation by plotting the graph between absorbance and compound concentration using UV-Vis spectrophotometer at predetermined known concentrations of ornidazole.

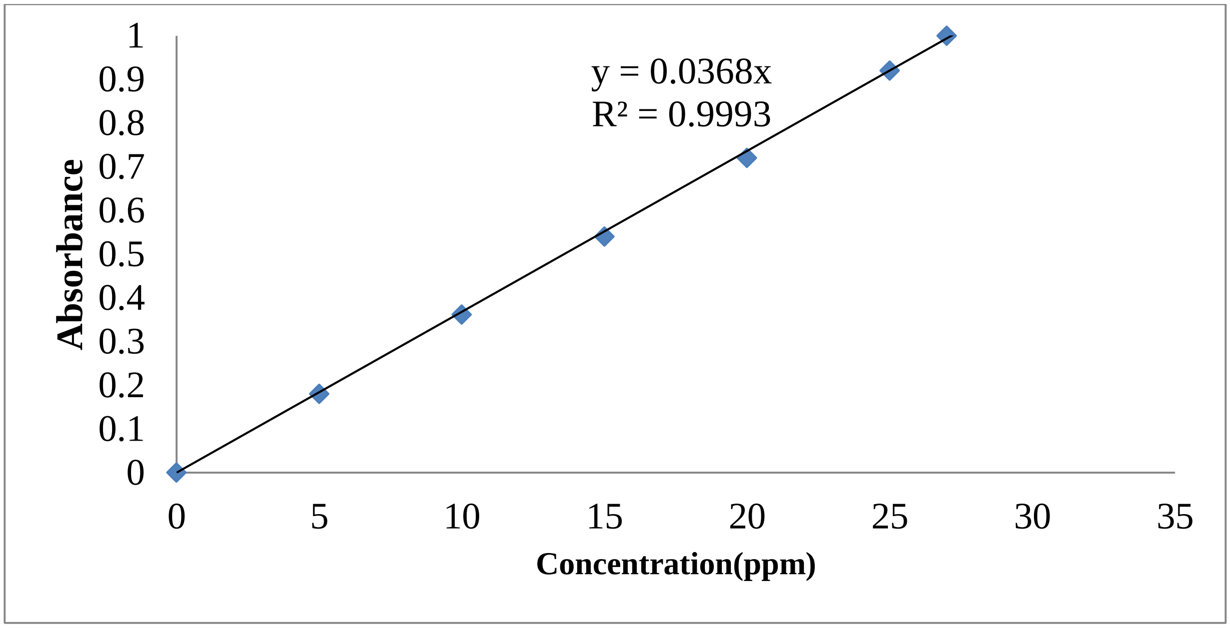


Fig 5.1: Calibration curve for ornidazole

5.1.2 Degradation of ornidazole by photocatalysis

The numbers of experiments were executed in order to model the photocatalytic degradation of ornidazole and to find the optimum conditions under UV light with varying pH, initial concentration of compound, time of degradation etc.

5.1.2.1 Modeling of photocatalytic process with ANN

ANN is an assuring modeling technique for photocatalytic degradation of non-linear relationship data sets, which are mostly encountered in photocatalytic degradation of pharmaceutical wastewater. Slurry mode experiments were used for the collecting the data for ANN modeling. Two types of ANNs mainly used are multilayered feed forward neural network trained by back-propagation algorithm and Kohonen self-organizing mapping for acquiring the appropriate weights. In the present study TiO_2 dose, pH, concentration of Ornidazole and time were used an input variables and % degradation of ornidazole was an output variable (Fig5.2).

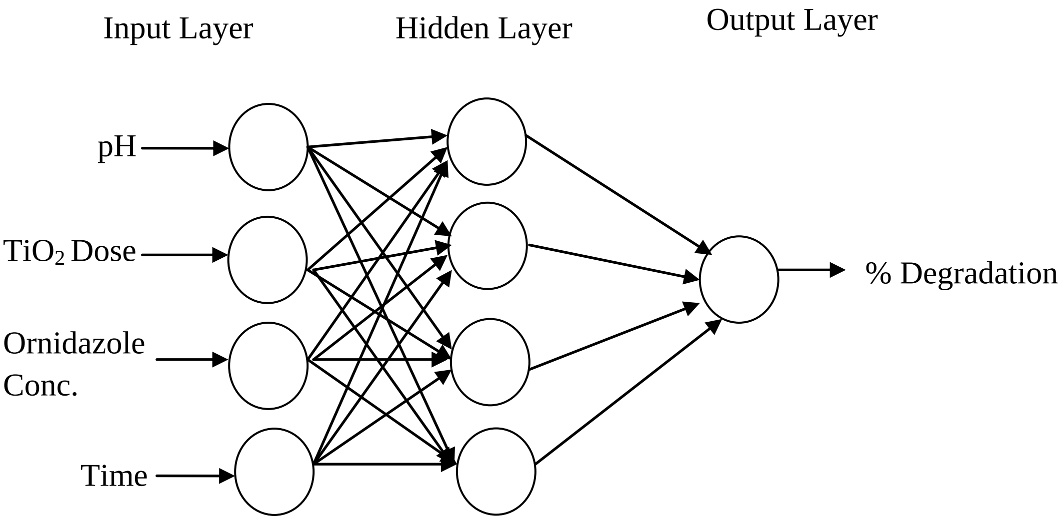
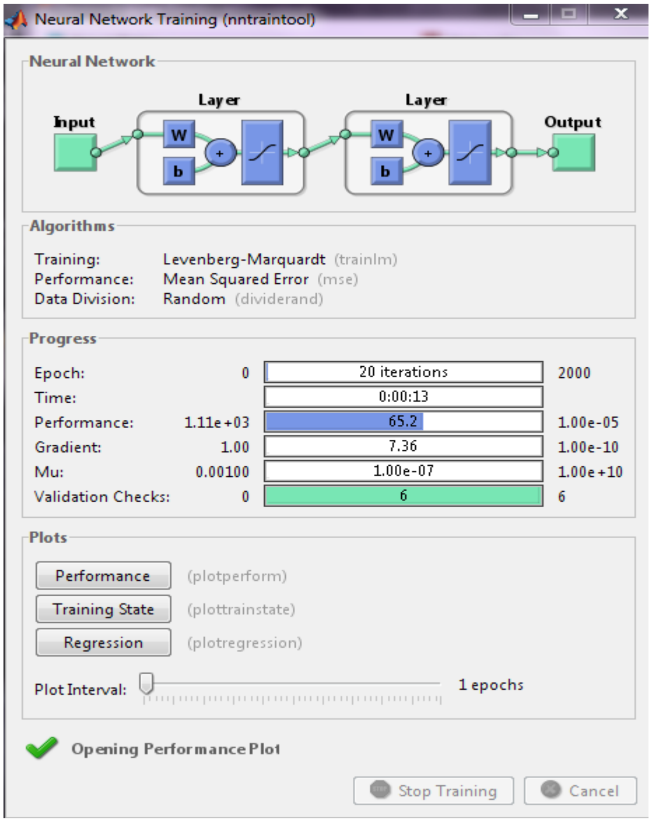


Fig 5.2: Schematic representation of ANN with input, hidden and output layers

Total 86 experiments were carried out and were used to provide it to the ANN structure. For the input to hidden layer mapping hyperbolic tangent ‘TANSIG’ (being a sigmoid transfer function) was used while for the hidden layer to the output layer mapping purely linear transfer function ‘PURELIN’ was used. The most important step of the ANN procedure is the selection of the topology i.e. optimum number of hidden layer neurons in the ANN function. For training the data sets containing 70 %, 15% for validation and 15% for testing of samples were used. Fig 5.3 showed the network training.



Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Epoch:	0	20 iterations	2000
Time:		0:00:13	
Performance:	1.11e+03	65.2	1.00e-05
Gradient:	1.00	7.36	1.00e-10
Mu:	0.00100	1.00e-07	1.00e+10
Validation Checks:	0	6	6

Plot Interval: 1 epochs

✓ Opening Performance Plot

Fig 5.3: Network training

Various tests of different topology were carried out to select optimum number of neurons, and the number of neurons was varied from 1 to 10. To avoid random correlation due to random initialization of weights each topology was repeated two times. Mean square error (MSE) was used as an error function. The Mean square error was found to be minimum for the four neurons as shown in Fig 5.4. Hence, four neurons were optimum for a single hidden layer to train the ANN network. To minimize the error between observed and predicted values back-propagation algorithm was used.

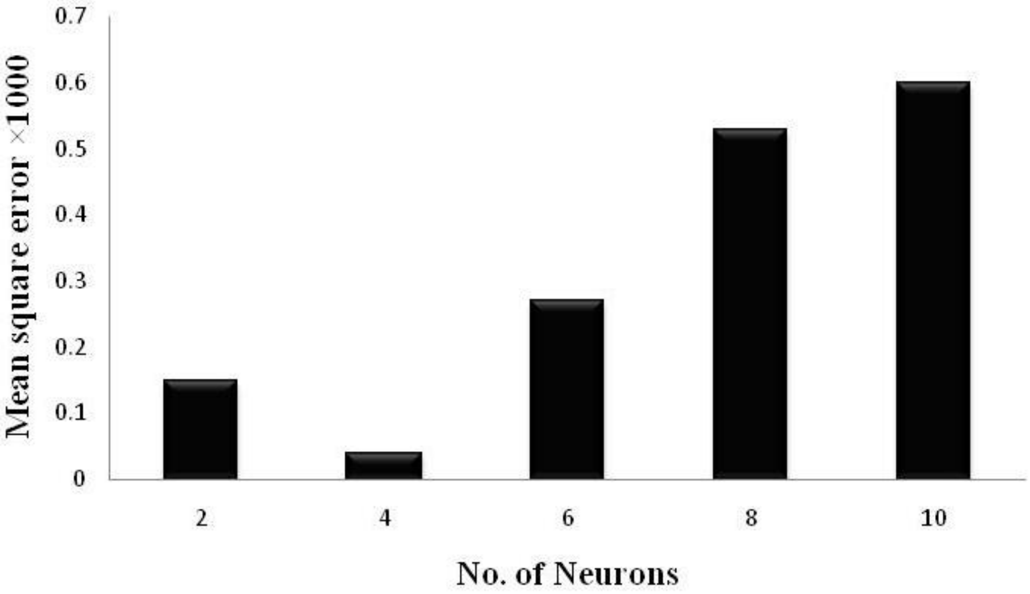


Fig 5.4: The effect of the number of neurons on the performance of neural network

The test sets and validation sets were randomly selected from the experimental data. The regression plots of the trained network are shown in Fig 5.5. The training of ANN modeling was done and R^2 value for training and validation was 0.968 and 0.916. This shows that model was ready for simulation. The accuracy of the network was tested with experimental values. The R^2 value for the network testing was 0.946, which shows that model was ready to simulate the output from given data inputs.

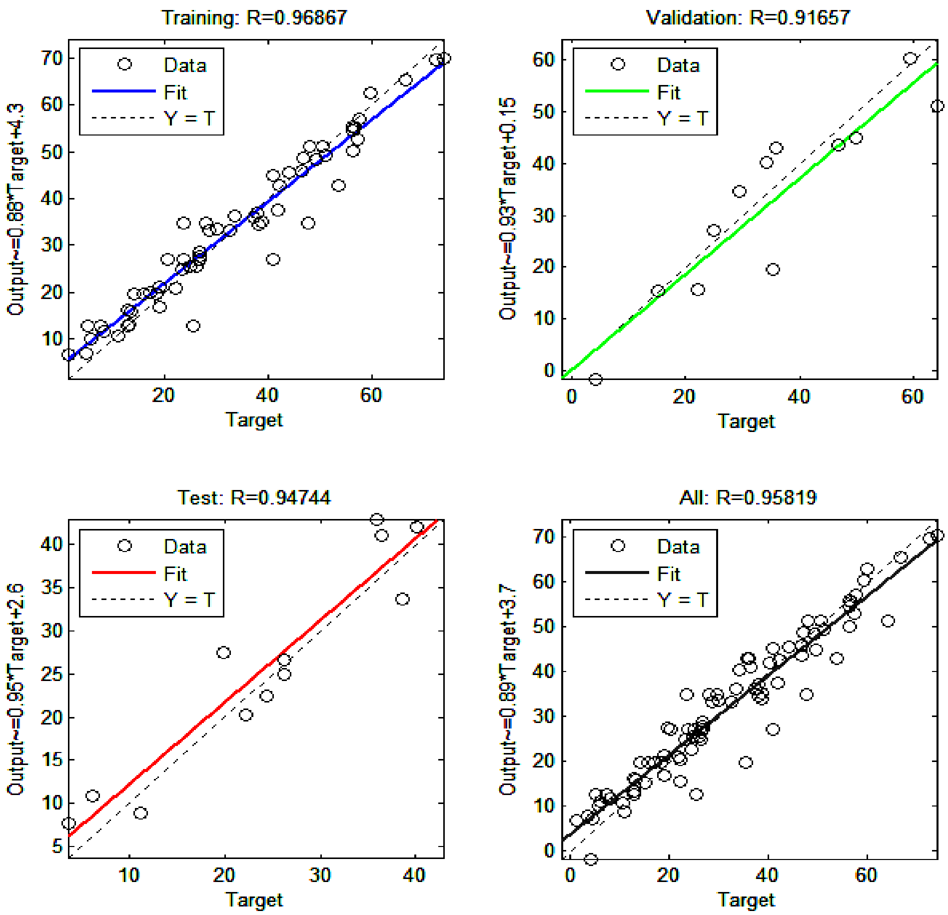


Fig 5.5: Regression analysis of training and target

The function sim was used to simulate the network. The output was predicted from a given input after stimulation of the network.

5.1.2.2 OPTIMIZATION by RSM

a) Box- Behnken Design (BBD)

Box-Behnken design under RSM (Response Surface Methodology) was used for the optimization of process parameters for photocatalytic degradation of wastewater containing ornidazole . The four operational parameters TiO_2 dose, pH, degradation time and compound concentration were used as input variables and % of degradation was taken as response. Table 5.1shows the various operational parameters and there levels.

Table 5.1: Range of variables and coded levels

Variables	-1	0	1
TiO_2dose(g/*l*)	0.4	1.2	2
pH	3	7	11
Ornidazole conc.(ppm)	10	20	30
Time(min.)	30	105	180

A full factorial design has been used to study the photocatalytic degradation of ornidazole and is shown in Table 5.2. The total of 29 experiments was suggested by BBD to optimize the process parameters such as TiO_2 dose, pH, concentration and time for % degradation of ornidazole.

Table 5.2: Full factorial BBD matrix used and simulated data from ANN's response

Std	TiO_2 Dose (g/*l*)	pH	Ornidazole conc.(ppm)	Time(min)	%Degradation
1	2	7	20	30	51.03
2	0.4	3	20	105	57.68
3	1.2	7	30	30	15.58
4	1.2	11	10	105	20.14
5	2	11	20	105	47.75
6	1.2	7	20	105	35.61
7	1.2	7	20	105	51.67
8	2	7	30	105	56.14
9	1.2	7	10	180	46.53
10	1.2	7	20	105	35.61
11	2	7	10	105	54.41
12	1.2	7	20	105	35.61
13	1.2	3	20	30	15.62
14	1.2	7	30	180	45.98
15	0.4	7	10	105	35.61
16	0.4	7	20	180	84.2
17	1.2	7	20	105	15.61
18	0.4	7	30	105	62.66
19	1.2	3	30	105	52.81
20	1.2	7	10	30	8.86
21	1.2	11	20	30	5.45
22	0.4	7	20	30	16.02
23	0.4	11	20	105	58.07
24	1.2	11	30	105	26.53
25	2	3	20	105	59.54
26	1.2	3	10	105	28.53

27	1.2	11	20	180	33.9
28	2	7	20	180	53.34
29	1.2	3	20	180	58.29

b) Statistical analysis

The % degradation of ornidazole wastewater by photocatalysis was simulated by ANN model according to the matrix of experiments designed as shown in Table 5.2. The sequential F-test and other adequacy measures were exploited for selecting the best Model. P value for the % degradation of ornidazole was found to be less than 0.01 so, quadratic model was suggested by sequential model sum of squares. Model summary statistics and sequential model sum of squares and were tested to decide the adequacy of model. A result of adequacy model was shown in Table 5.3 for % degradation of ornidazole. Sequential model sum of squares showed that quadratic model was best fit model for experimental data for % degradation of ornidazole. Cubic model was found to be aliased for degradation of ornidazole.

Table 5.3: Sequential model sum of squares for % degradation of ornidazole

Source	**Sum of Squares**	**DF**	**Mean Square**	**SD**	**R^2 value**	**Adjusted R^2**	**Predicted R^2**	**F value**	**Prob>F**	
Mean	47105.06	1	47105.06							
Linear	4569.70	4	1142.43	15.55	0.4406	0.3473	0.1617	4.73	0.0059	
2FI	1425.86	6	237.64	15.59	0.5780	0.3436	0.2264	0.98	0.4685	
Quadratic	3462.90	4	865.72	8.08	0.9119	0.8238	0.7576	13.26	<0.0001	Suggested
Cubic	238.64	8	29.83	0.9349	0.6963	0.6202	3939.46	0.27	0.9562	Aliased
Residual	675.07	6	112.51							
Total	57477.23	29	1981.97							

Where SD is Standard Deviation

The Prob > F value was 0.0001, which indicates that quadratic model is significant. The coefficient of determination is 0.91 for quadratic model. This concludes a good correlation between observed and predicted values. The difference between predicted values and observed values dividing by standard error of the residual has close relation with % Normal probability.

This advocates a good correlation between the observed and predicted values as shown in Fig 5.6. The predicted values were closer to the actual values.

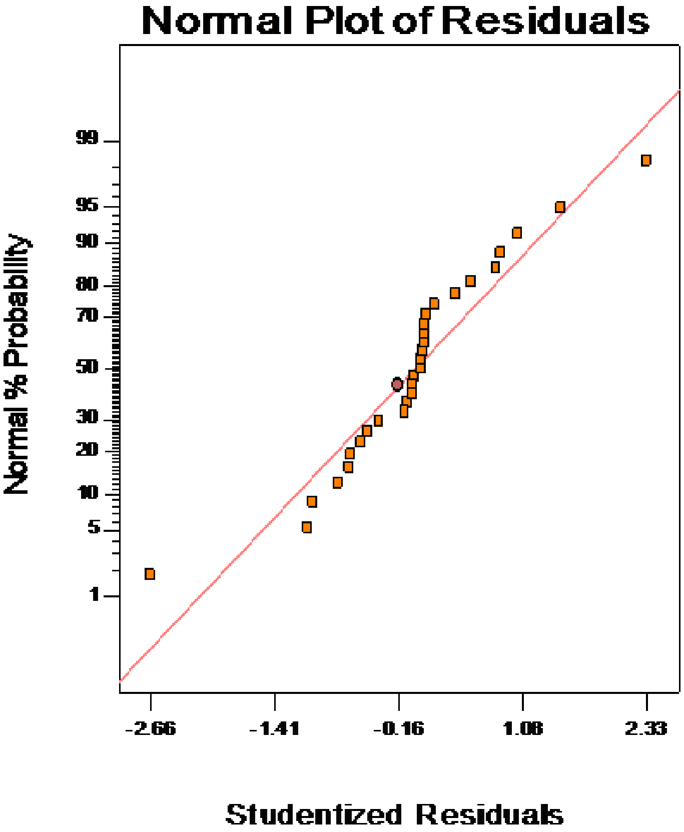


Fig 5.6: Residual plot for photocatalysis of % degradation of ornidazole

The ANOVA (analysis of variance) shows the model F-value for %degradation of ornidazole is 10.35164 as shown in Table 5.4. This showed that model considered is significant for % degradation of ornidazole. For model terms to be significant, “prob>F” values should be less than 0.05 “prob>F” values larger than 0.100 indicates that model term are insignificant.

From ANOVA it is clear that the time and (TiO_2 dose)^2 are highly significant terms for %degradation of ornidazole.

Table 5.4: ANOVA suggested by BBD for the % degradation of ornidazole

	% degradation of ornidazole					
Source	Sum of Squares	DF	Mean Square	F Value	Prob>F	
Model	9458.453	14	675.6038	10.35164	<0.0001	Highly Significant
TiO_2 Dose	5.293408	1	5.293408	0.081106	0.7800	
pH	541.7664	1	541.7664	8.300973	0.0121	
Ornidazole conc.	358.832	1	358.832	5.498043	0.0343	
Time	3663.809	1	3663.809	56.13706	<0.0001	Highly Significant
TiO_2 Dose ^{2}	2779.574	1	2779.574	42.58877	<0.0001	Highly Significant
pH^2	4.327892	1	4.327892	0.066312	0.8005	
Ornidazole conc. ^{2}	29.5138	1	29.5138	0.452212	0.5122	
$Time^2$	131.6775	1	131.6775	2.017569	0.1774	
TiO_2 Dose×pH	37.0881	1	37.0881	0.568266	0.4634	
TiO_2Dose× Oridazole conc	160.2756	1	160.2756	2.455751	0.1394	
TiO_2 Dose×Time	1084.714	1	1084.714	16.62005	0.0011	
pH× Ornidazole conc.	80.01303	1	80.01303	1.225964	0.2869	
pH×Time	50.5521	1	50.5521	0.774562	0.3937	
Ornidazole conc.×Time	13.21323	1	13.21323	0.202454	0.6596	
Residual	913.7158	14	65.26541			
Lack of Fit	258.8969	10	25.88969	0.158149	0.9916	Not Significant
Pure Error	654.8189	4	163.7047			
Cor Total	10372.17	28				

c) Effect of TiO_2 dose, pH, time and concentration on %degradation of ornidazole

To study the effect of parameters i.e. TiO_2 dose, pH, concentration of compound and time on % degradation of ornidazole(response) for photocatalysis of pharmaceutical compound, the three dimension response surface graph were considered.

$(TiO_2)^2$ concentration and time was highly significant for present study. It can be observed that %degradation increases with increase in TiO_2 dosage from 1.20 to 2 for pH value from 3 to ≈5as shown in Fig 5.7(a). While at lower pH and lower TiO_2 dose % degradation of ornidazole was maximum. It could also be observed that increasing in TiO_2 dose with increasing ornidazole concentration marginally affect %degradation of ornidazole. But at lower TiO_2 dose with lower ornidazole concentration %degradation was maximum. The TiO_2 dose ≈0.8 to 1.20 at all ornidazole concentration were showing constant effect on %degradation as shown in Fig 5.7(b). The ornidazole concentration was kept constant for the photocatalytic degradation as its concentration in the fresh water is in the range of 20 mg/*l*. It could be seen that value of t ≈ 67 min to 80 min always increases %degradation. But at the lower TiO_2 dose the degradation of ornidazole was maximum. The increase in time above 80 min marginally decreases the degradation of ornidazole as shown in Fig 5.7(c).

Photocatalytic degradation of any component was done by the $OH^{\bullet}$ attack, direct oxidation by h^+ and direct reduction by the e^- in the conduction band. This is depends upon the pH and the dose of TiO_2 with respect to the time. TiO_2 suspended in aqueous mode with the help of irradiation having energy greater than the band-gap energy of the semiconductor produces h^+_{TiO2} and e^-_{TiO2}. The migration of holes generated and electrons generated oxidants, which further participate in the degradation of the ornidazole. From regression analysis, it was concluded that in acidic condition at the lower dose of TiO_2 % degradation of ornidazole was more. This was because of the structural properties of the ornidazole. Ornidazole might be directly disintegrated by hydrogen chloride cleavage and dehydrogenation (Zhao et al. 2012). The process of interaction of TiO_2 and ornidazole was schematically explained in Fig 5.8.The catalyst behavior can be explained by TiO_2 surface charge density. TiO_2 is amphoteric in nature which helps in interacting with the degrading component (Saggioro et al. 2011). The TiO_2 carries net zero charge at pH 6.8. Under alkaline conditions ($pH \geq 6.8$) TiO_2 surface is negatively charged and in acid media ($pH \leq 6.8$) the TiO_2 surface is positively charged. Taking in account the structure of ornidazole, an excess positive charge on the TiO_2 surface promotes a strong interaction with Cl^- group of the ornidazole (Fig 5.8a). The excess negative charge promotes the repulsion of the ornidazole by the titanium surface, diminishing the catalytic activity of this semiconductor (Fig 5.8b). This hypothesis agrees that the degradation reaction was occurred on the surface of TiO_2 or close to the surface of TiO_2 but surface and not in the solution. It was concluded that in acidic pH, TiO_2 surface was easily available for the degradation reaction of ornidazole. So, at acidic pH and lower dose of TiO_2 was effective to degrade ornidazole effectively.

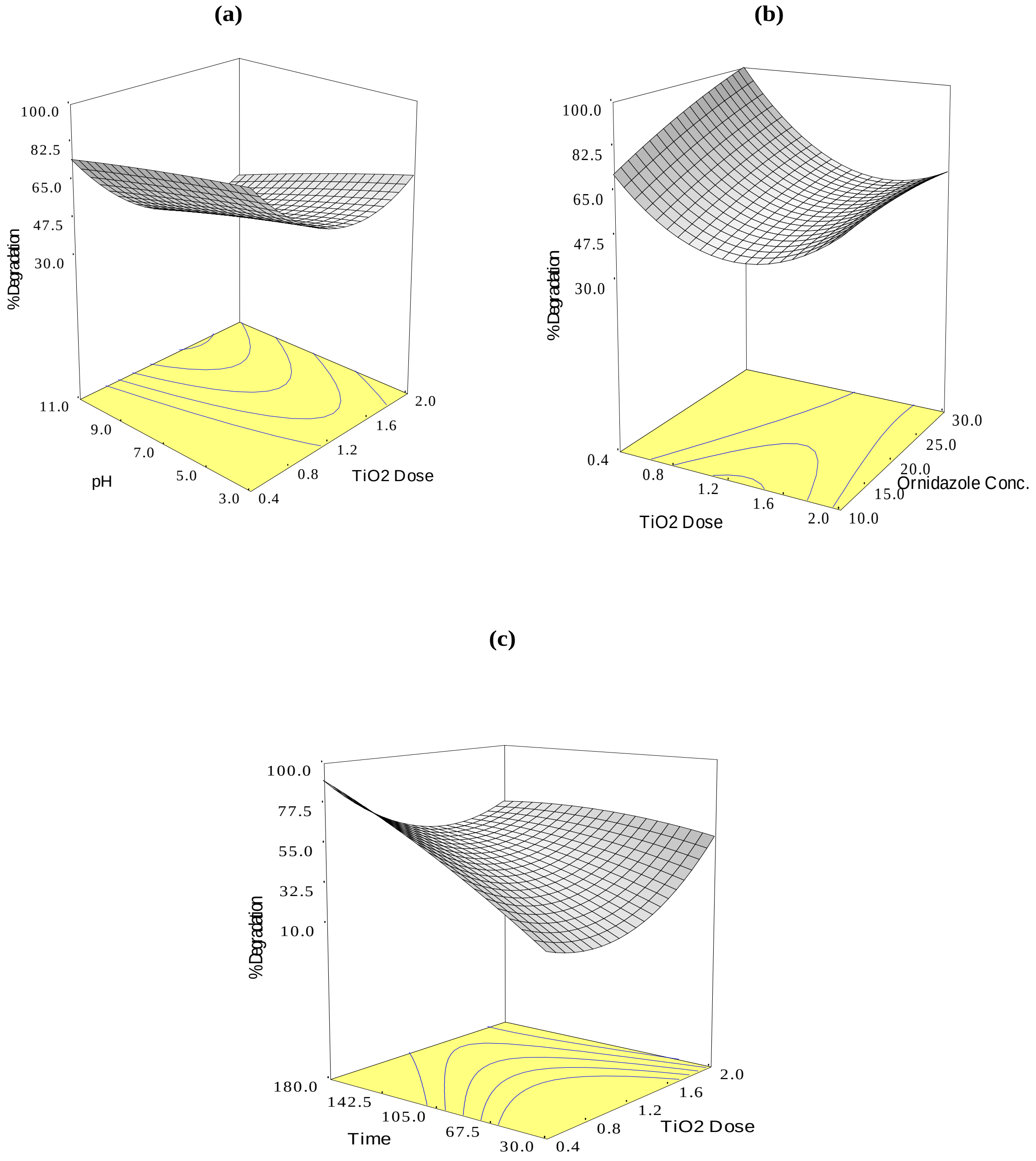


Fig5.7: % degradation of ornidazole 3-D response surface graph **(**a) %degradation 3-D response surface graph between TiO_2 dose and pH (b) % degradation of ornidazole3-D response surface graph between TiO_2 dose and ornidazole concentration (c) % degradation of ornidazole3-D response surface graph between TiO_2 dose and time

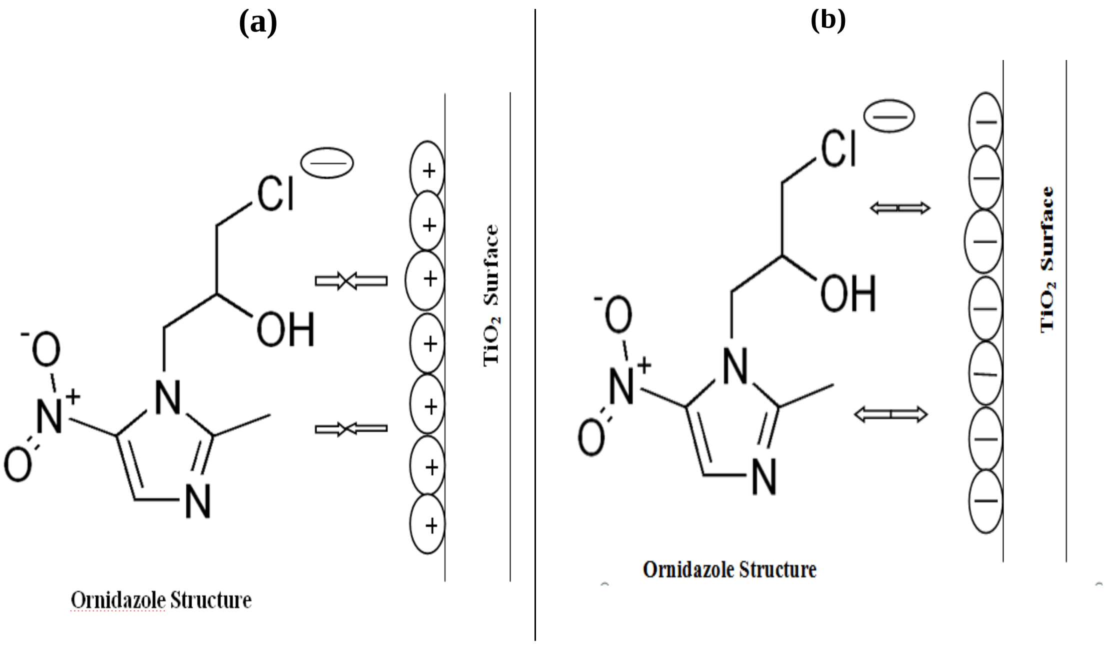


Fig 5.8: Schematic interaction model of ornidazole and TiO_2: (a) acid sites and (b) basic sites

d) Optimization analysis

Photocatalysis of Ornidazole was optimized by BBD as %degradation of ornidazole wastewater was maximized. For this consideration some constraints for operational parameters were applied as shown in Table 5.5.

Table 5.5: Constraints applied for optimization processes

Variables	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
TiO_2 dose(g/*l*)	is in range	0.4	2	1	1	3
pH	is in range	3	11	1	1	3
Ornidazole conc.(ppm)	is in range	10	30	1	1	3
Time(min.)	is in range	30	180	1	1	3

In this study, % degradation of ornidazole was optimized in terms of maximization using BBD. The values of optimum parameters were found to be TiO_2 dose= 0.43 g/*l*, t= 175 min and pH=3.31, desirability of D = 0.99 was produced. At this optimum condition, the % degradation of ornidazole suggested by BBD was to be 86.02% for ornidazole concentration of 20 ppm as shown in Table 5.6.

Table 5.6: Optimum conditions for photocatalytic degradation of ornidazole wastewater

Variables	Optimum values
pH	3.31
Time(t)	175mins
TiO_2 Dose	0.43 g/*l*

e) Confirmation Results

Optimum condition for photocatalytic treatment of Ornidazole wastewater was verified experimentally. Experiment was run for 175mins at pH 3.31 and initial concentration was 20ppm. The % degradation of ornidazole is 77.70%. The optimization results of RSM take care of interactions between process parameters and the predictions agreed well with the experimental and ANN results.

5.1.2.3 Kinetic study

The kinetics of photocatalytic treatment of ornidazole wastewater was studied for at optimum conditions obtained from BBD through RSM. In present study, first order model and second order model were tested. To the experimental data obtained from photocatalytic process at optimum conditions (TiO_2 dose = 0.4g/*l*, pH = 3.31, t= 175 min) second order model was fitted for % degradation of ornidazole according to the rate equation.

$$\frac{-dC}{dt} = k_1 C^2 \tag{14}$$

On integrating between known limits and rearranging, the above model becomes

$$\frac{1}{C_t} = \frac{1}{C_0} - \kappa t \tag{15}$$

Where, C_o initial concentration of ornidazole at zero time, C_t concentration of ornidazole at any time, t degradation time (min), κ second order rate constant (l mg^{-1} min^{-1}). At optimum condition, the degradation of ornidazole was followed second order of kinetics as shown in Fig 5.9. The R^2 value for kinetic study was 0.99 with rate constant value of 0.001 *l* mg^{-1} min^{-1}.

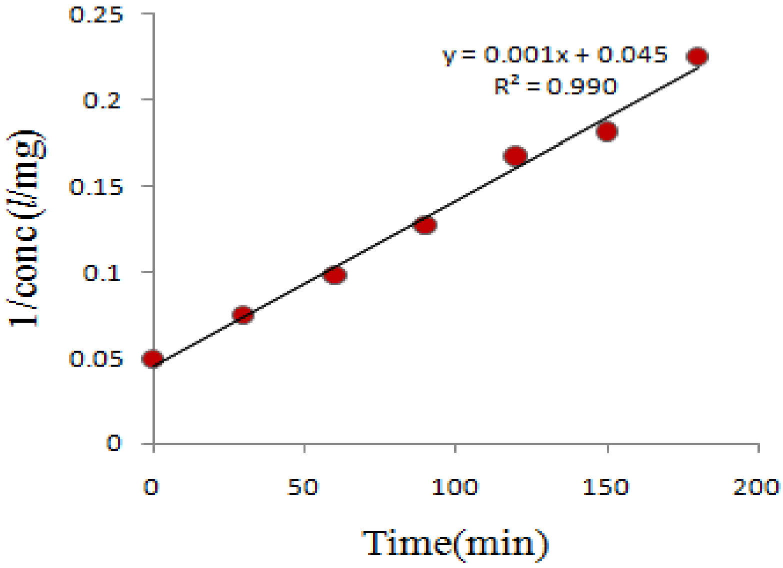


Fig 5.9: kinetic study of degradation of ornidazole

5.1.2.4 Bioassay test

The toxicity test of the treated ornidazole waste water was carried out using E-Coli DH-α strain. The test was conducted using zone inhibition method, which is also called Kirby-Bauer method. The culture was kept in incubator for 24 hours at 37 ^{0}C. After 24 hrs it was found that there was no zone of inhibition existed as shown in Fig 5.10.The E-Coli DH-α strain is a test microorganism strain in the laboratory. It is a sensitive strain towards toxic compounds. If there was no zone of inhibition, then it shows the complete mineralization of the synthetic ornidazole effluent.

Fig 5.10: Bioassay test of ornidazole wastewater

5.1.2.5 Fixed bed study

Several complications such as agglomeration of the particles during the process are caused due to usage of TiO_2 in the form of nano-particles, which reduces the efficiency of photocatalytic process. Hence, recovering of nano particles from waste water by TiO_2 slurry needs costly microfiltration processes (Rastegar et al. 2012). Light transport limitation appears with a high catalyst loading. Besides, it is difficult to separate the small TiO_2 particles from water after treatment where the particle size of fine P25 Degussa TiO_2 powders is about 21nm and where, in the aqueous phase, the particles form aggregates within the micron range. Hence a fixed bed reactor was used to avoid these problems. This, however, may lower the oxidation potential per volume of water compared to the dispersed-phase system, due to mass transfer limitation and light transport limitation caused by (i) the presence of substrate that absorbs light and worsens and (ii) a lower catalyst surface-to-volume ratio. In this experiment we used cement beads to support the TiO_2 nanoparticles.

With the slurry TiO_2 system, an additional process step would need to be entailed for post-separation of the catalysts. This separation process is crucial to avoid the loss of catalyst particles and introduction of the new pollutant of contamination of TiO_2 in the treated water.

Hence, immobilization of catalyst was done on cement beads. The process was carried out in fixed bed reactor. For Fixed bed reactor the time taken for the degradation at pH 3.31 was 360 minutes at the flow rate of 500m*l*/h. The percentage degradation was found to be 76.5%. The plot for the % degradation of ornidazole wastewater with respect to time has been shown in Fig 5.11 With increase in time it could be seen that till 180 minutes the degradation of ornidazole wastewater is increasing and it reached nearly 70%.But after that with increase in time it could be observed that the degradation remains nearly constant.It increases at very slow rate. The maximum degradation observed was 76.5%.

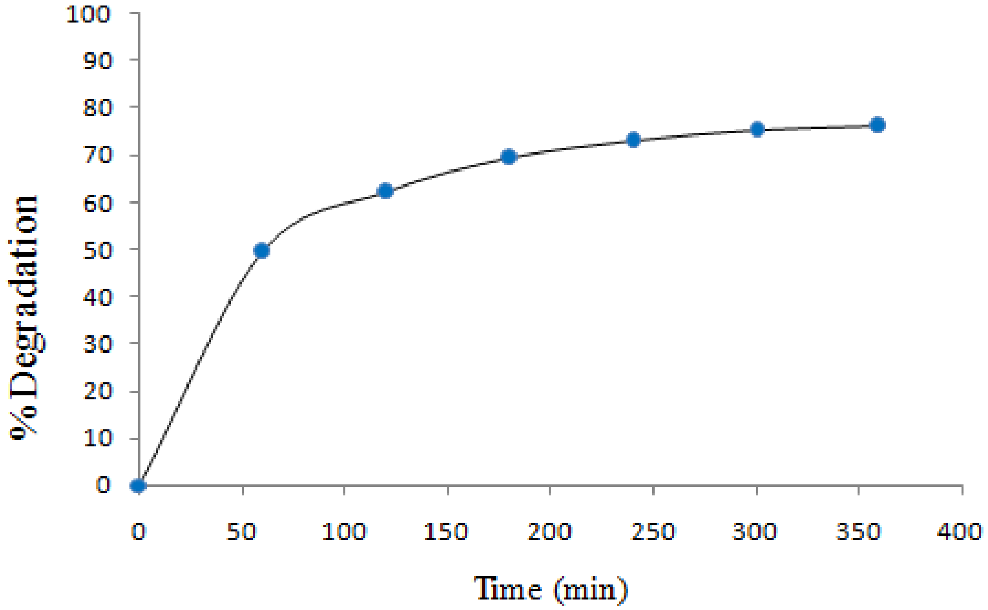


Fig 5.11: %degradation of ornidazole wastewater in the Fixed bed reactor

5.2 REAL PHARMACEUTICAL WASTEWATER

5.2.1 Photocatalytic degradation of real pharmaceutical wastewater

The numbers of experiments were executed in order to find the optimum conditions for the photocatalytic degradation of real wastewater under UV light with varying pH, TiO_2 dose and time of degradation etc.

5.2.1.1 Characterization of treated wastewater

The real pharmaceutical wastewater was investigated for its general characteristics such as TSS, TDS, pH, BOD and COD. The Table 5.7 shows the characterization of the untreated real pharmaceutical wastewater.

Table 5.7: Characterization of treated real pharmaceutical wastewater

Parameters	**Concentration(mg/*l*)**
Total suspended solids(TSS)	3180
Total Dissolved solids(TDS)	160
Total solids(TS)	3340
pH	5.8
Biochemical oxygen Demand	1727
Chemical oxygen demand	12425
Dissolved oxygen(DO)	0.1

5.2.1.2 RSM optimization

a) Box- Behnken Design (BBD)

Box-Behnken design which is based on RSM was used for this experimental design. The three operational parameters were variable TiO_2 dose, pH and degradation time were used as input variables and % of COD removal was taken as response. Table 5.8 shows the various operational parameters and there levels.

Table 5.8: Range of variables and coded levels

Variables	-1	0	1
TiO_2dose (g/*l*)	0.5	1.5	2.5
pH	3	7	11
Time (Min.)	30	255	480

The total 17 number of experiments were conducted as suggested by RSM to explore the effect of three parameters TiO_2 dose, pH and time on % COD removal. Full factorial design used to study the photocatalytic degradation of real pharmaceutical waste is shown in Table. 5.9

Table 5.9: Full factorial BBD matrix

Std	pH	TiO_2 Dose(g/*l*)	time(min)	%COD removal
1	3.00	2.50	270.00	45
2	7.00	2.50	60.00	15
3	7.00	1.50	270.00	35
4	3.00	1.50	480.00	56.61
5	7.00	0.50	480.00	55.81
6	11.00	1.50	60.00	17
7	11.00	1.50	480.00	48
8	7.00	0.50	60.00	14
9	7.00	1.50	270.00	35
10	7.00	1.50	270.00	35
11	3.00	0.50	270.00	57
12	3.00	1.50	60.00	19
13	11.00	0.50	270.00	41
14	7.00	2.50	480.00	57
15	7.00	1.50	270.00	35
16	7.00	1.50	270.00	35
17	11.00	2.50	270.00	43.7

b) Statistical analysis

The % COD removal (response) of pharmaceutical wastewater by photocatalysis of real waste water was calculated according to the arrangement of operational parameters in a design matrix of experiments and results are shown in Table 5.9. For selecting the best Model the sequential F-test and other adequacy measures were used. P value for the % COD removal was found to be less than 0.01 so, quadratic model was suggested by sequential model sum of squares. Model summary statistics and Sequential model sum of squares were used to decide the adequacy of model. A result of adequacy model was shown in Table.5.10 for % COD removal. Sequential model sum of squares showed that quadratic model was best fit model for experimental data for response % COD removal as shown in Table 5.10. Cubic model were found aliased for % COD removal.

Table 5.10: Sequential model for % COD removal

Source	**Sum of Squares**	**DF**	**Mean Square**	**SD**	**R^2 value**	**Adjusted R^2**	**Predicted R^2**	**F value**	**Prob>F**	
Mean	24405.33	1	24405.3					25.06	<0.0001	
Linear	3007.67	3	1002.56	6.33	0.852	0.8185	0.7028	0.48	0.7062	
2FI	64.95	3	21.65	6.75	0.871	0.7936	0.3845	0.48	0.7062	
Quadratic	404.21	3	134.74	2.70	0.985	0.9670	0.7688	18.50	<0.0001	Suggested
Cubic	50.98	3	16.99	0	1.000	1.0000	-	6.366×10^7	<0.0001	Aliased
Residual	0	4	0							
Total	27933.14	17	1643.1							

Where SD is Standard Deviation

Prob > F value was 0.0001, which showed that fitted quadratic model is significant. It could be seen that the values of R^2 , adjacent R^2 and predicted R^2 was 0.985, 0.967, 0.768 for quadratic model which indicated that model is significant.The model gives coefficient of determination (R^2) value 0.98 as shown in Table 5.10. This showed a good correlation between predicted values and observed values. The cubic model was found to be aliased. The difference between predicted values and observed values dividing by standard error of the residual has close relation with % Normal probability. This indicated a good correlation between the predicted and observed values as shown in Figure 5.12. The predicted values of % COD removal were closer to the actual value of % COD removal.

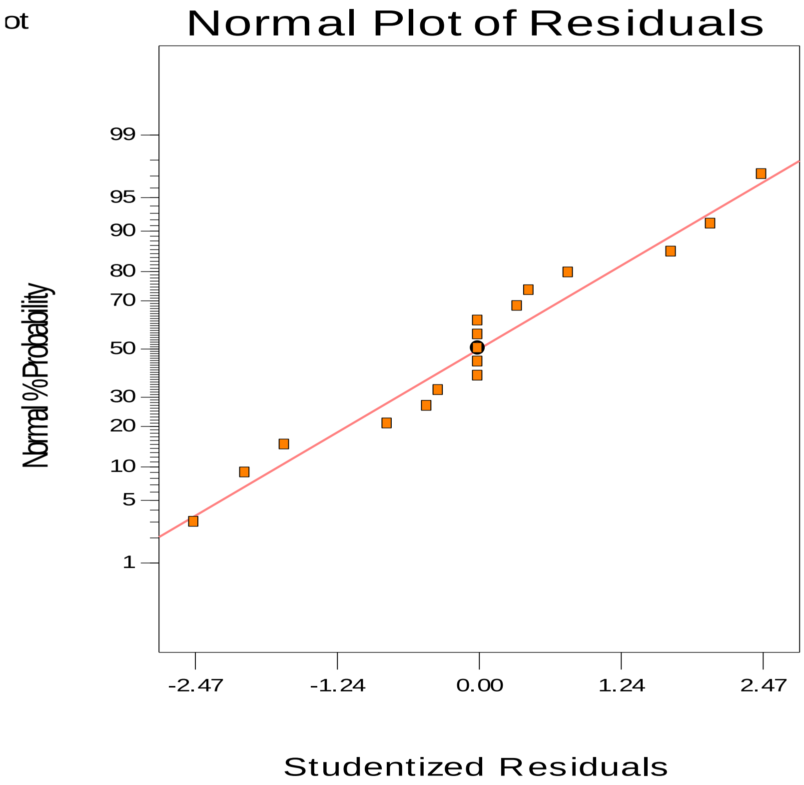


Fig 5.12: Residual plots for photocatalysis of real waste % degradation.

The ANOVA described the model F-values for %degradation has been shown in Table 5.11. It was observed that the model F value is 53.05 which confirmed that this model is significant for %COD removal. For model terms to be significant, “prob>F” values should be less than 0.05 and “prob>F” values greater than 0.100 showed that model term are insignificant. The time is highly significant variable for the % COD removal of real pharmaceutical wastewater.

Table 5.11: Analysis of variance implied by BBD for the % COD removal of real pharmaceutical wastewater

	% COD removal					
Source	Sum of Squares	DF	Mean Square	F Value	Prob>F	
Model	3476.83	9	386.31	53.05	<0.0001	Highly Significant
Ph	6.32	1	6.32	13.37	0.0081	
TiO_2 Dose	2903.98	1	2903.98	0.87	0.3826	
Time	97.37	1	97.37	398.77	<0.0001	Highly Significant
pH^2	136.20	1	136.20	18.70	0.0035	
TiO_2 Dose ^{2}	150.95	1	150.95	20.73	0.0026	
$Time^2$	128.99	1	128.99	17.71	0.0040	
pH×TiO_2Dose	54.02	1	54.02	7.42	0.0296	
pH×Time	10.92	1	10.92	1.50	0.2603	
TiO_2Dose.×Time	9.025×10^{-3}	1	9.025×10^{-3}	1.239×10^{-3}	0.9729	
Residual	50.98	7	7.28			
Lack of Fit	50.98	3	16.99			
Pure Error	0.000	4	0.000			
Cor Total	3527.81	16				

c) Effect of TiO_2 dose, pH and time on % COD removal

Photocatalytic degradation of any component was done by the $OH^{\bullet}$ attack, direct oxidation by h^+ and direct reduction by the e^- in the conduction band. This is depends upon the pH and the dose of TiO_2 with respect to the time. TiO_2 suspended in aqueous mode with the help of irradiation having energy greater than the band-gap energy of the semiconductor produces h^{+}_{TiO2} and e^{-}_{TiO2}. The migration of electrons and the holes generate oxidants which further participate in the degradation of the real pharmaceutical effluent. Regression analysis of degradation of the pharmaceutical effluent was studied. The effect of TiO_2 dose and pH on the % COD removal with respect to change in time was studied. With the increase in time at lower dose of TiO_2 in acidic pH, the % COD removal was maximum. But with the increase in the dose of TiO_2 at acidic pH gradually decreases the % COD removal along with increase in time. At higher pH and lower TiO_2 dose, the % COD removal becomes minimum. But at higher TiO_2 dose and basic pH marginally reduces the % degradation. As shown in Fig 5.13(a) the pH 6 to ~ 8 the % COD removal was minimum and it showed no effect with increase in time. The higher dose of TiO_2 of ~1.5 to 2 gm/l at basic pH showed marginal increase on the % COD removal with the increase in time. Fig 5.13(b) showed that the response of time and pH on the % COD removal with respect to change in TiO_2 dose. When there was increase in time at lower pH % COD removal was maximum but pH after 4 to basic leads to decrease in % COD removal with increase in time with respect to decrease in TiO_2 dose. Fig 5.13(c) showed the effect of time and TiO_2 dose on the % COD removalwith respect to change in pH. It was perceived that at lower pH and lower dosage of TiO_2 the % COD removal leads to the maximum. At the TiO_2 dose of 1 to ~1.7 gm/*l* the % COD removalwas minimum. But after 1.7 gm/*l* of TiO_2 dose with increase in time % COD removal gradually increases. From regression analysis, it was concluded that in acidic condition at the lower dose of TiO_2 % COD removal of real pharmaceutical wastewater was more. At higher concentration of TiO_2 in basic pH % COD removal of real pharmaceutical effluent was marginally lower at acidic pH. This was because of the structural properties of the TiO_2. The catalyst behavior can be explained by TiO_2 surface charge density. TiO_2 is amphoteric in nature which helps in interacting with the degrading component (Saggioro et al. 2011). The TiO_2 carries net zero charge at pH 6.8. Under alkaline conditions ($pH \geq 6.8$) TiO_2 surface is negatively charged and in acid media ($pH \leq 6.8$) the TiO_2 surface is positively charged. Taking into account the structure of pharmaceutical effluent, excess charge which is positive on the TiO_2 surface promotes a strong interaction with negative groups of the pharmaceutical effluent. An excess negative charge of pharmaceutical effluent promotes the catalytic activity of this semiconductor. This hypothesis agrees that the degradation reaction was occurred on the surface of TiO_2 or close to the surface of TiO_2 but surface and not in the solution. It was concluded that in acidic pH, TiO_2 surface was easily available for the degradation due to the excess negative charge in pharmaceutical effluent. But in basic pH interaction between the catalyst and positive charged groups were less due to less amount of positive charge available. So, at acidic pH and lower dose of TiO_2 was effective to degrade pharmaceutical effluent effectively.

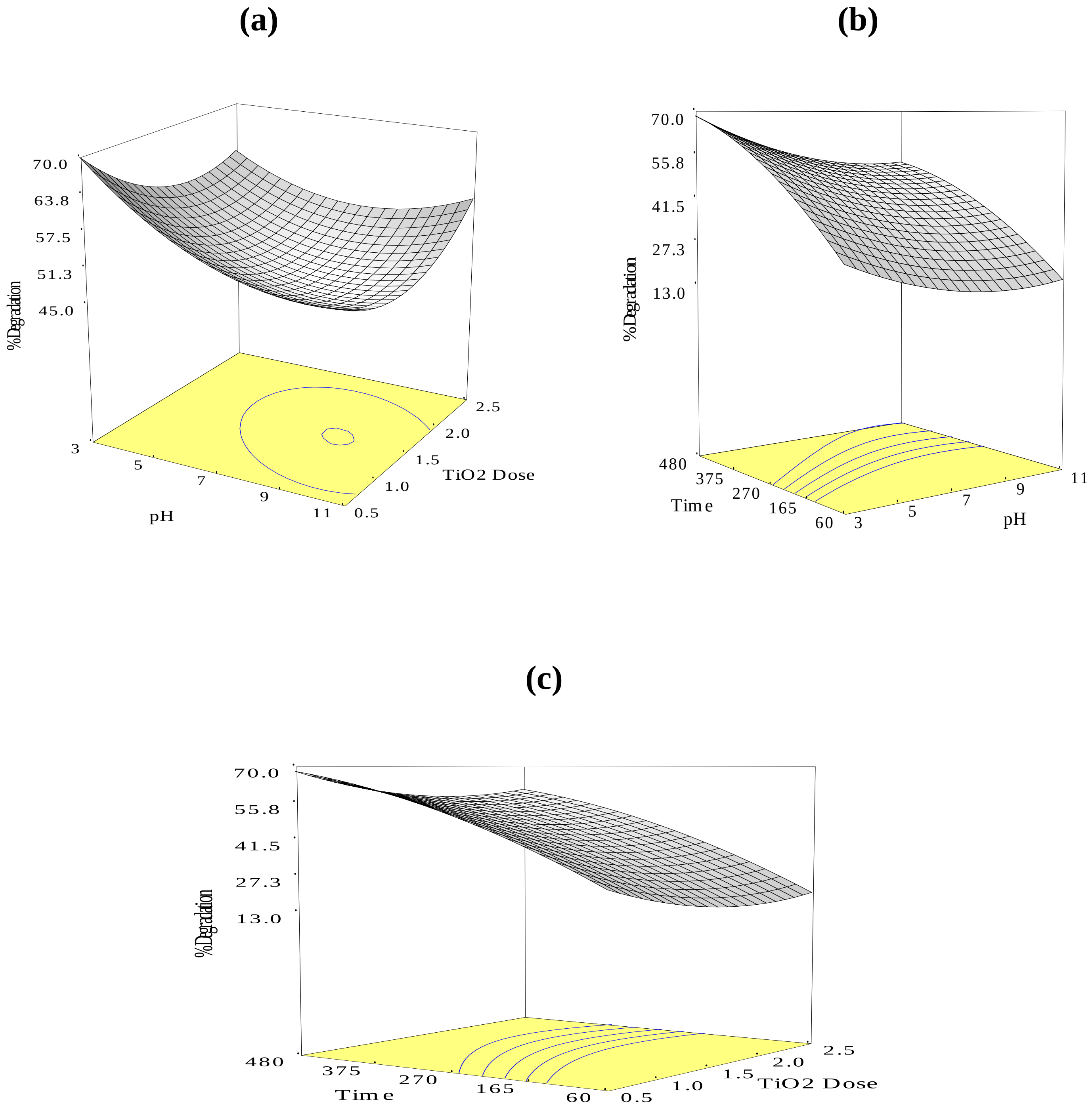


Fig5.13: % COD removal three dimension response surface graph **(**a) % COD removal three dimension response surface graph between pH and TiO_2 dose (b) % COD three dimension response surface graph between pH and time(c) % COD removal three dimension response surface graph between TiO_2 dose and time

d) Optimization analysis

Process parameters for photocatalytic treatment of real pharmaceutical wastewater were optimized by RSM by maximizing % COD removal. For this consideration some constraints for operational parameters were applied as shown in Table 5.12. Lower and higher limits were set for the operating parameters.

Table 5.12: Applied constraints for optimization processes

Variables	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
pH	is in range	3	11	1	1	3
TiO_2 dose(g/*l*)	is in range	0.5	2.5	1	1	3
Time(min.)	is in range	30	180	1	1	3

In this study, % COD removal was maximized using BBD. The values of parameters which were optimized were found to be TiO_2 dose= 0.60g/*l*, t= 455 min and pH=3.20, producing the desirability of D = 0.99 (Table 5.13).The % COD removal at the optimum condition suggested by BBD was to be 67.02%.

Table 5.13: Optimum conditions for photocatalysis of real pharmaceutical wastewater

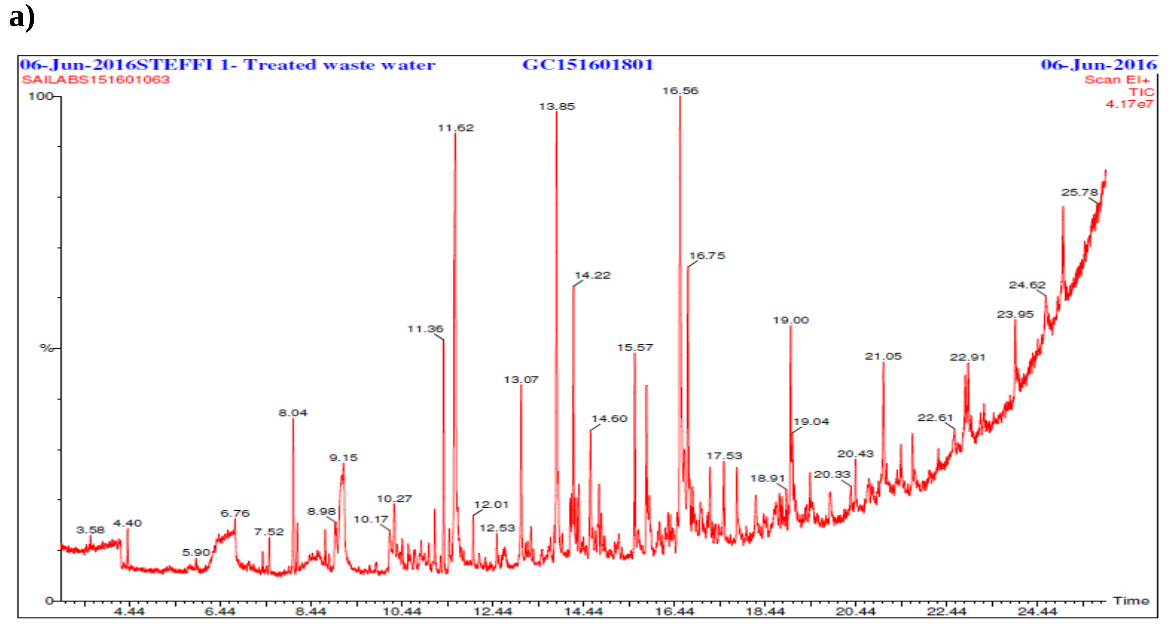
Variables	**Optimum values**
pH	3.20
Time(t)	455mins
TiO_2 Dose	0.60 g/*l*

e) Confirmation results

Optimum condition for photocatalytic treatment of real pharmaceutical wastewater was verified experimentally. Experiment was run for 455 mins at pH 3.20 and TiO_2 dose of 0.60 g/*l*. The % COD removal is 63.7%. Hence, the predictions agreed well with the experimental and ANN results. The optimization results by RSM also take care of interactions between process parameters.

f) Mineralization

Mineralization of compound during photocatalytic treatment is important. In this context, COD reduction was study for the mineralization of real wastewater. With optimized conditions, 63.7% reduction of COD was achieved after eight hours. Moreover, Gas chromatograms (Fig 5.14) and absorbance curves (Fig 5.15) indicated the disappearance of peaks for different compounds.



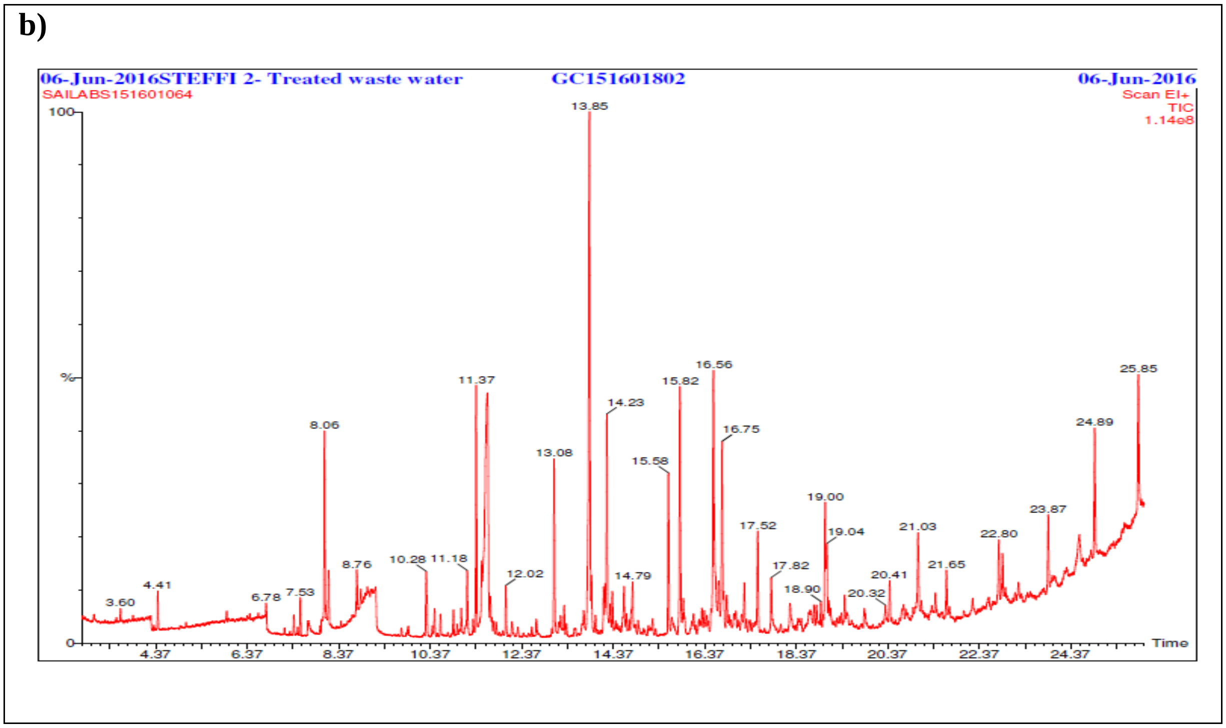


Fig 5.14: Shows chromatograms for a) untreated real pharmaceutical wastewater, b) treated real pharmaceutical wastewater

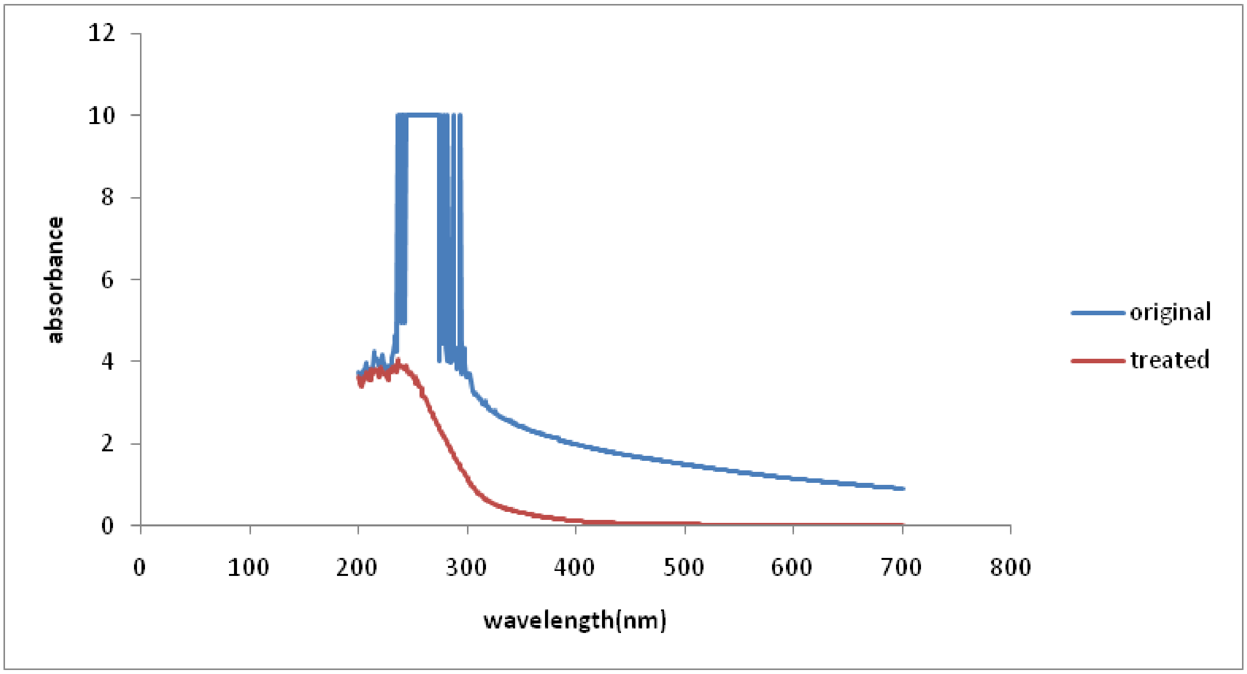


Fig 5.15: Shows absorbance for a) initial untreated real pharmaceutical wastewater, b) treated real pharmaceutical wastewater

It could be observed from the GCMS analysis that the peaks present at the retention time of 11.62, 14.62, and 16.56 were demolished after treatment. The compounds matched are dodecamethyl Cyclohexasiloxane, 5-(trimethylsilyloxy)indane, turmerone respectively. These compounds are mostly used in antibiotics. Dodecamethyl cyclohexasiloxane is used for the personal care products and for skin infections, 5-(trimethylsilyloxy)indane for diabetes, obesity, hyperlipidemia, and atherosclerotic diseases and turmerone for bacterial infections as shown in Table 5.14 (a). Compound present at retention time of 4.40 i.e deoxyleurosidine is used in Antitumor alkaloid and is toxic which after treatment got degraded into Hexane, 2,4-dimethyl which is used in asthamatic problems and is non toxic. Many other compounds are present in the real wastewater which degrades into different compounds which are non toxic as shown in Table 5.14 (b).

Absorbance was taken for the real waste water and treated waste water. It could be seen that most of the compounds are degraded.

Table 5.14 a: List of various compounds identified with GC-MS Analysis in Untreated pharmaceutical wastewater

S.No	Compound	Retention Time	Molecular Mass	Molecular Formula	Matching %	Uses and Comment
1.	N-1-(2-methoxy-propenylidene)t-butylamine	7.37	141	$C_8H_{15}ON$	78.8%	It is used as a counter ion in drug substance and is highly toxic
2.	Decane ,Octadecane	7.51/8.04/ 11.36/ 13.07/ 14.22	142, 254	$C_{10}H_{22}$, $C_{18}H_{38}$	80.9%/ 94.2%/95.7% /93%/95.2% 	It used as adsorbent and in paraffin waxes for encapsulation
3.	Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester	8.98/13.85/15.82	370	$C_{16}H_{30}O_4Si_3$	79.4%/86% /84.5%	It is used to treat Skin irritant
4.	Decamethyl Cyclopentasiloxane,	9.15/11.62	370	$C_{10}H_{30}O_5Si_5$	83.5%/92.6%	It is used in skin treatment drugs, personal care products
5.	Tetrasiloxane, 3,5-diethoxy-1,1,1,7,7,7-hexamethyl-3,5-bis	13.85	518	$C_{16}H_{46}O_7Si_6$	86%	It is used for encapsulation
6.	5-(trimethylsilyloxy)Indane	14.60	206	$C_{12}H_{18}OSi$	79%	It is used for Diabetes, obesity, hyperlipidemia, and atherosclerotic diseases.and is toxic

7.	Butyl 2,4-dimethyl-2-nitro-4-pentenoate,	15.57	229	$C_{11}H_{19}O_4N$	97.8%	It is a suspected respiratory toxicant and is suspected to be neurotoxic.Antiasthmatics Bronchodilators
8.	AR-Turmerone,	16.56	216	$C_{15}H_{20}O$	95.1%	It is used as Antibacterial agents
9.	Docosane,	16.75	310	$C_{22}H_{46}$	92.5%	It is used as Adsorbent, Phase change material
10.	(2R,3R,4R,5S,6R,8S,10S)-5-Acetoxy-10-benzyloxy-8 benzyloxymethyl-2	19.00/21.05	498	$C_{29}H_{38}O_7$	95.2%/94%	It is used as Antiinflamatory drug
11.	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-Hexadecamethyl-octasiloxane	22.91/23.95/25	578	$C_{16}H_{50}O_7Si_8$	82%/89.7% 91.2%	It is used for encapsulation

Table 5.14 b: List of various compounds identified with GC-MS Analysis in untreated pharmaceutical wastewater

S.No	Compound	Retention Time	Molecular Mass	Molecular Formula	Matching %	Uses and Comment
1.	Hexane, 2,4-dimethyl	4.41	114	C_8H_{18}	82.9%	It is used as a drugs for antiasthma
2.	Decane,Octadecane	7.39/8,06/10.28/11.27/14.23/21. 05/	142, 254	$C_{10}H_{22}$, $C_{18}H_{38}$	86.7%,95.3%/94.6%/96.3%/95.9%/94.3%	It used as adsorbent and in paraffin waxes for encapsulation (present in original waste)

3.	11-ethyl-3-methyl-5,9-dioxa-7-Pentadecanol	7.52	274	$C_{16}H_{34}O_3$	89.4%	It is used as a Perfumed indegrient
4.	Cyclohexasiloxane, dodecamethyl	11.62	444	$C_{12}H_{36}O_6Si_6$	94.9%	It is used in skin treatment drugs,personal care products
5.	Cycloheptasiloxane, tetradecamethyl-	13.85	518	$C_{14}H_{42}O_7Si_7$	88.2%	It is used in skin treatment drugs
6.	Pentadecane	15.57	212	$C_{15}H_{32}$	97.1%	It is used as an antibiotic
7.	Silicate anion tetramer	15.87	888	$C_{24}H_{72}O_{12}Si_{12}$	88.4%	It is used infood liquid carbonated
8.	Beta-Tumerone,	16.56	218	$C_{15}H_{22}O$	96.1%	It is used as Antibacterial agents (presemt in original waste)
9.	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-octasiloxane	21.64,22.88,23.87,24.89,25.85	578	$C_{16}H_{50}O_7Si_8$	85.6%/97.8%/90.7%,90%,92.9%	It is used for encapsulation (presemt in original waste)
10.	(R,R)-3,8-dimethyldecane, Butyl 2,4-dimethyl-2-nitro-4-pentenoate	22.88	578	$C_{16}H_{50}O_7Si_8$	97.8%	It is used as food and flavor indegrient

5.2.1.3 Characterization treated pharmaceutical wastewater

The treated pharmaceutical wastewater was investigated for its general characteristics such as TSS, TDS, pH, BOD and COD. The Table 5.15 shows the characterization of the treated pharmaceutical wastewater.

Table 5.15: Characterization of treated pharmaceutical wastewater

Parameters	Concentration(mg/*l*)
Total dissolved solids(TDS)	1460
Total suspended solids(TSS)	100
Total solids(TS)	1560
pH	5.80
Biochemical Oxygen Demand (BOD)	2100
Chemical oxygen demand	4097
Dissolved oxygen(DO)	0.1

5.2.1.4 Kinetic study

The kinetics of real pharmaceutical wastewater was studied for photocatalytic process at optimum conditions obtained from BBD through RSM. In present study, first order model and second order model were tested. To the experimental data obtained from photocatalytic process at optimum conditions (TiO_2 dose = 0.6g/*l*, pH = 3.20, t= 455 min) second order model was fitted for real waste water degradation according to the rate equation.

$$\frac{-dC}{dt} = k_1 C^2 \qquad (16)$$

On integrating between known limits and rearranging, the above model becomes

$$\frac{1}{C_t} = \frac{1}{C_0} - \kappa t \qquad (17)$$

Where, C_o initial concentration of real waste water at zero time, C_t concentration of real waste water at any time, t degradation time (min), κ second order rate constant (l mg^{-1} min^{-1}). At optimum condition, the degradation of real wastewater followed second order of kinetics as shown in Fig 5.16. The R^2 value for fitted data is 0.99 with rate constant value of 3×10^{-7} l mg^{-1} min^{-1}.

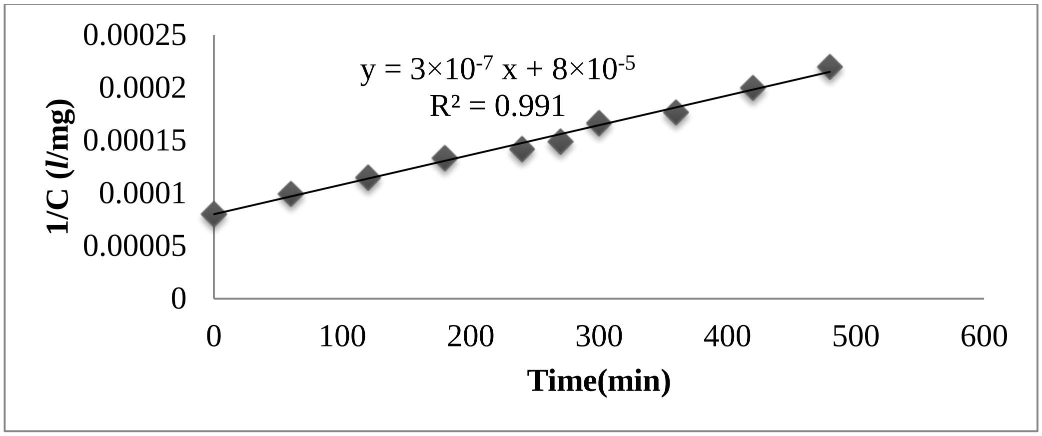


Fig 5.16: kinetic study of degradation of real wastewater

5.2.1.5 Bioassay test

The toxicity test of the treated and untreated real pharmaceutical wastewater was carried out using E-Coli DH-α strain. The test was conducted using zone inhibition method which is also called Kirby-Bauer method. The culture was kept in incubator for 24 hours at 37 ^{0}C. After 24 hrs it was found that there was no zone of inhibition existed as shown in Fig 5.17.The E-Coli DH-α strain is a test microorganism strain in the laboratory. It is a sensitive strain towards toxic compounds. If there was no zone of inhibition, then it showed the complete mineralization of the effluent. It was found that the untreated pharmaceutical wastewater was toxic as zone of inhibition existed but after photocatalytic treatment there was no zone of inhibition and it could be concluded that the treated real pharmaceutical wastewater is non toxic in nature.

Fig 5.17: Bioassay test of treated real pharmaceutical wastewater

CHAPTER 6

CONCLUSION

Heterogeneous photocatalysis process is a promising technique and an eco-friendly method 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.

In the present study the heterogeneous photocatalytic degradation for the pharmaceutical compound ornidazole and real pharmaceutical wastewater with UV/TiO_2 was assessed.

Pharmaceutical compound Ornidazole has been successfully degraded in the presence of TiO_2 photocatalyst. Modeling for the ornidazole by photocatalytic treatment was done using ANN and optimized neurons for the treatment were found to be four. The R^2 value for training, validation and testing was 0.968, 0.916 and 0.946 respectively. This showed that the model was trained properly and is ready to predict the results. For optimization BBD was used. The values of R^2 for BBD was 0.9119, which indicated that model was significant. It was examined that photocatalytic process was an efficient process for degradation of ornidazole at lower pH and lower TiO_2 dose with the increase in time. The %degradation of ornidazole was optimized. The optimum conditions of parameters were found to be TiO_2 dose= 0.43g/*l*, t= 175 min and pH=3.31, which showed an overall desirability of 0.99. At optimum condition the % degradation of ornidazole suggested by BBD was 86.02. To verify the adequacy of experiments conformational experiment was performed. Experimentally % degradation of ornidazole at optimum conditions was found to be 77.70 % for slurry mode reactor. Second order kinetics was followed for the photocatalytic treatment of wastewater containing ornidazole. The toxicity test showed the growth of microorganisms after 24 hrs. This was concluded that the by-products formed after the photocatalysis of ornidazole are not toxic. The effluent was safe for disposal into the environment.

Treatment of real pharmaceutical wastewater has been carried out with variation in parameters like pH, catalyst dose and time. Optimization of the data was done using BBD. The values of R^2 for BBD was 0.985 which indicated that model was significant. It was observed that photocatalytic process was an effective process for degradation of real wastewater at lower pH and lower TiO_2 dose with the increase in time. The % COD removal was optimized. The optimum conditions obtained were TiO_2 dose= 0.60g/*l*, t= 455 min and pH=3.20, which showed an overall desirability of 0.99. At this optimum condition, the % COD removal suggested by BBD was to be 66.12. To verify the adequacy of experiments conformational experiment was performed. Experimentally % COD removal at optimum conditions was found to be 63.70 % for slurry mode reactor. The toxicity test showed the growth of microorganisms after 24 hrs. This was concluded that the untreated pharmaceutical waste was toxic but by-products formed after the photocatalysis of real pharmaceutical wastewater are not toxic. The effluent was safe for disposal into the environment.

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