Photocatalytic Degradation of Pharmaceuticals Wastewater

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

of

Masters of Sciences

In

Chemistry

Submitted By

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Under the Supervision of

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CERTIFICATE

I here by declare that the Dissertation 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 Sciences** in Chemistry at School of chemistry and biochemistry, **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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DECLARATION

I, the undersigned, hereby declare that the research work presented in M.Sc. Dissertation entitled **"Photocatalytic degradation of pharmaceuticals wastewater"** has been carried out by me under the supervision of **Dr. V. K. Sangal**, Associate Professor, Chemical Engineering Department, Thapar University, Patiala.

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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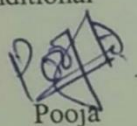

Pooja

ABSTRACT

Heterogeneous photocatalysis process has proven its points of interest over traditional strategies for wastewater treatment. In the present study the heterogeneous photocatalysis treatment was applied for degradation of the pharmaceutical wastewater of cetirizine by using TiO_2 as photocatalyst. The experiments were run in slurry mode and fixed mode. The input parameters which were differed are pH, cetirizine concentration, TiO_2 dose and time. Optimization was performed by using RSM. The experiments were performed at the optimized condition for fixed bed treatment utilizing TiO_2 immobilized on pumic stone. At the optimized conditions pH=3.35 and TiO_2 dosage 2.32g/*l* obtained from RSM the % degradation was observed to be 98.38% for slurry mode for 410 minutes and for fixed bed the % degradation was 71.5% for 600 minutes. The results concludes that at the lower flow rate the % degradation was maximum. Because at lower flow rate wastewater is getting more time to remain in contact with photocatalyst due to which degradation occurs. Kinetic study showed that degradation of cetirizine follows first order kinetics with rate constant value $k = 0.007\ min^{-1}$. The results demonstrates that the predictions agreed with the experimental results.

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ABBREVIATIONS

- AOPs- Advanced Oxidation Processes
- 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)
- Fig- Figure
- gm - Gram
- h_{vb}^{+} - holes(valance band)
- hr- hour
- IUPAC - International Union of Pure and Applied Chemistry
- Kg - Kilogram
- L - litre
- m - Metres
- M - Moles
- m^{2} - Meters square
- m^{3} - Meters cubic
- mg - Milligram
- min^{-1} - Per minute
- µL - Microlitre
- nm - Nanometres
- OH^{-} - Hydroxyl ion
- $OH^{\bullet}$ - Hydroxyl radical
- ppm - Parts per million
- RSM-Response Surface Methodology
- TiO_{2}- Titanium Oxide
- UV- Ultraviolet

Chapter 1

Introduction

1.1 General

Water is essential requirement for our day by day life activities domestic, industrial and commercial activities. Around two thirds of the Earth's surface area is covered by 1,386 million cubic kilometers (km^3) water. As life standards improve, consumption of water level also increase that results in increase of wastewater generation also which originates from many sources. Ground water and surface water when comes in wastewater sources add a volume to it. The treatment of wastewater is decided by its characteristics and source. Domestic wastewater contains vegetable waste, scum, detergents waste whereas wastewater from an industrial process may include toxic chemicals and metals, organic and radioactive wastes. The wastewater is treated to prevent problems caused by it in environment which makes water no longer suitable for appropriate utilization[1].

1.2 Contaminant of concern in wastewater

The most widely recognized industries like textile, pharmaceutical, pesticides and other organic chemicals manufacturing execrate wastewater. Some substances present in wastewater can be extremely dangerous like nitrogen which on high temperature and pH turn out to be more lethal to both flora and fauna existing on this planet [2]. Poisonous substance traces like chlorine when released into streams, oceans even in little amount can be harmful to aquatic life. Water contamination is making water bodies like lakes, rivers, oceans, aquifers and groundwater impure. This contamination of water bodies occurs when toxics substances are directly or indirectly released into it without any treatment.

1.3 Pharmaceuticals as a pollutant

India is one of highest producers of pharmaceutical wastewater with 4th rank in terms of volume. Most commonly utilized pharmaceuticals are antibiotics, antidepressants, anti-inflammatory and analgesics which are not used inside the body and 90% of the medicines is excreted which can enter in water bodies by mean of household or industrial discharges. The Associated Press recently reported that the concentrations found in pharmaceuticals in Indian plants are 150 times more detected in the U.S. The utilization of most generally prescribed drugs on a large scale draw consideration towards the best possible treatment ways for degradation of pharmaceutical wastewater .Even they are only found at trace level which raises the issue of human well being and the environment[3].The cause and courses of pharmaceutical products in environment as shown in Fig1.1.

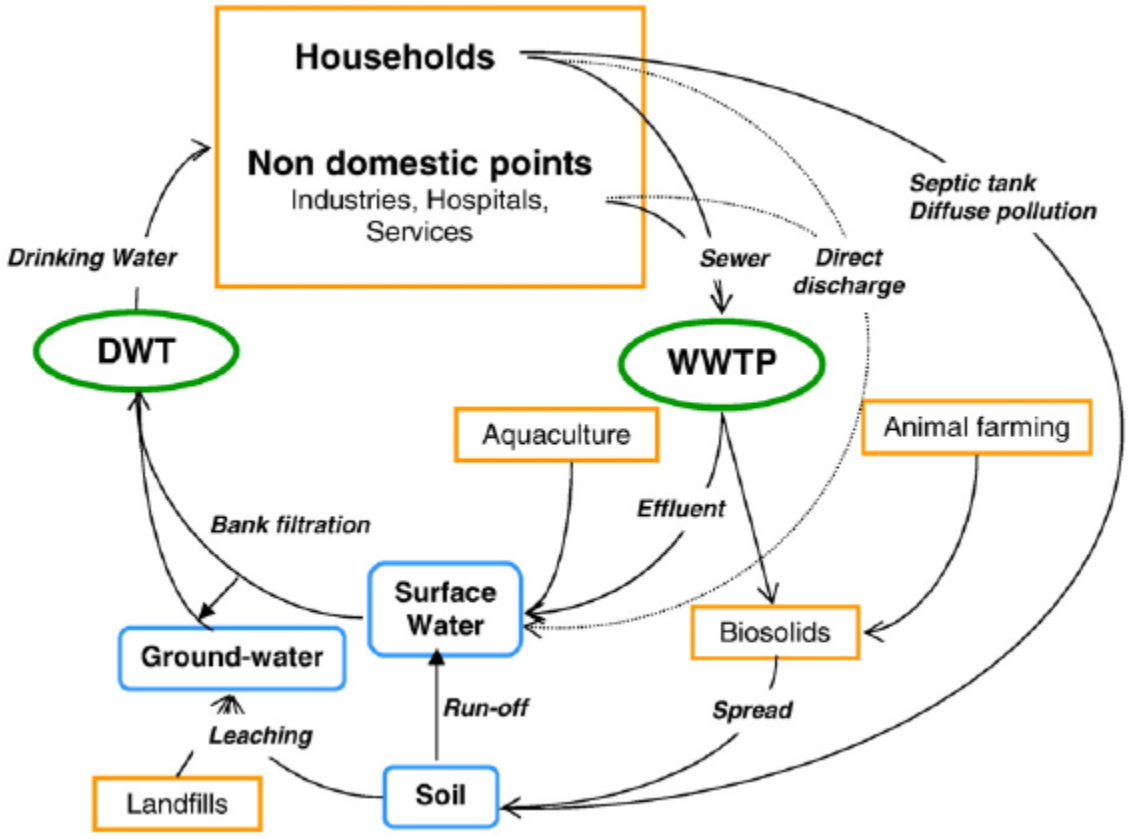

Fig1.1: Cause and routes of Pharmaceutical Products[4]

1.4 Standards for pharmaceutical industries

As environmental regulations become more strict, a proper treatment of effluent is required before releasing wastewater. Research and development for the advancement of wastewater treatment are constantly under process due to genuine reasons of concern towards environment but conventional and existing treatment techniques in pharmaceutical industry experiences issues to evacuate the contaminants according to the government release norms given in Table 1.1.

Table 1.1: National Environmental Quality Standards (NEQS) of Pharmaceutical Effluent Rule, 2001

	Parameter	Concentrations not to exceed limits in mg/l
Compulsory	pH	6-10
	Oil & Grease	10
	Chloride (as Cl)	1000
	Ammonia	40
	Total suspended solids	250
	Total dissolved solids	3500
Additional	Mercury	0.01
	Cyanide	0.1
	Arsenic	0.2

Note: All values are according to CPCB standard

1.5 Conventional Methods

Conventionally used methods like primary treatment and biological method does not cause any awful impacts on ecological system . However, the generation of lot of sludge, high energy utilization and operational issues including foaming, color and bulking in secondary clarifiers are related with activated sludge plants.

This clearly demonstrates that the traditional treatment methods are not that much productive for totally evacuating a large amount of the contaminations present in wastewaters. More

particular techniques are required for degradation of these non biodegradable organic compounds.

So, advanced oxidation processes (AOPs) are of major interest now days as AOPs not only remove organic and inorganic toxins but also for effectively diminishing lethality with complete mineralization.

Chapter 2

Advanced oxidation processes

2.1 Introduction

Wastewater treatment plants are intended to expel pollutants, for example solids and biodegradable organic compounds. But these plants are not design to evacuate small traces of pollutants which are resistant to conventional wastewater treatments. Advanced oxidation processes are treatments which are considered to be effective even for removing these small traces from wastewater. Advanced existing treatment technology is inadequate for the removal of micro pollutants as they are not intended for this particular class of toxins. These failures of conventional waste water treatment plants for expelling pharmaceuticals raise the urgent concern for innovation of technology that can be viably utilized for these compounds.

Advanced oxidation processes are considered as best suitable methods to degrade pollutants present in wastewater which are known to be non-biodegradable or have low biodegradability. Advanced oxidation processes for wastewater treatment include photolysis, photocatalysis, ozonation Fenton and Photo-Fenton, ultrasound radiation, sonolysis, electrochemical oxidation, and wet air oxidation. Oxidation Technology has been examined to solve this environmental problem. Different types of advance oxidation processes are as shown in Fig 2.1 below.

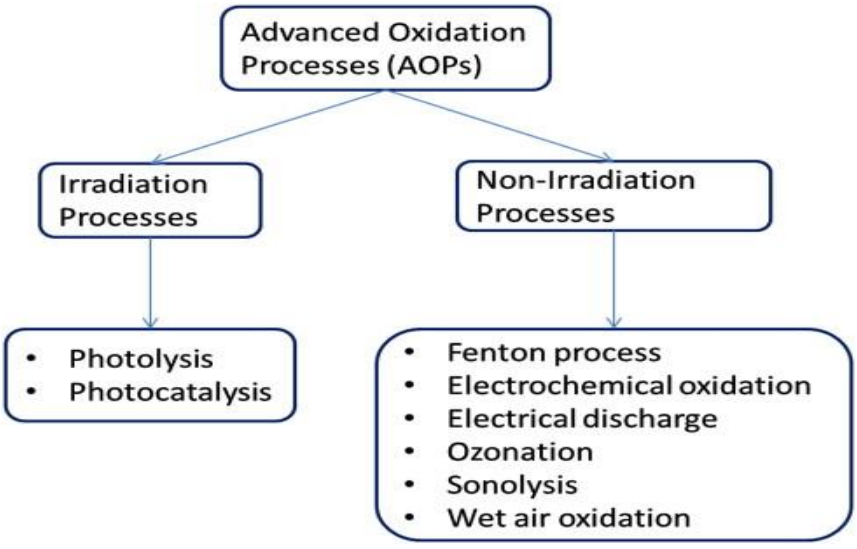

Fig 2.1: Different types of AOPs

All Advanced oxidation processes are described as degradation of organic and inorganic pollutants particles present in wastewater. The oxidant species which have high oxidizing power are generated in these processes. The hydroxyl radical actively participates in advance oxidation processes[5] .

2.2 Photocatalytic degradation

As per the IUPAC photochemical degradation is defined 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 remove pollutants and eventually total mineralization to carbonate species (CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}), water and mineral acids (HX).

2.3 Heterogeneous photocatalysis

Heterogeneous photocatalysis in presence of a semiconducting photocatalyst used as an AOP for the treatment of wastewater [6] containing inorganic and organic toxins exhibit very low concentration. It is very promising for solving the environmental problems in the most economic way[7]. Photocatalysis by titanium dioxide has turned into an extremely dynamic field of research now days for the degradation of toxins present in wastewater. TiO_2 has proven to be the most efficient semiconductor photocatalyst because it is stable, non harmful, inert chemically, cheap, highly resistant to photo corrosion and highly reactive in ultraviolet (UV) light[8]. Photocatalytic oxidation is an advanced oxidation process in which titanium dioxide (TiO_2) is used as a semiconducting photocatalyst and ultraviolet (UV) irradiation ($\lambda \leq 380$ nm) as a light source to produce charge carriers which react with species which are adsorbed on their surface to generate a highly reactive OH^o identify as the most powerful oxidant. In the previous couple of years, a few endeavors have been placed in expanding the the TiO_2 surface area by dispersing nano-particles of TiO_2 on high surface area materials like pumic stone, active carbon, zeolites and silica gels.

2.4 Mechanism of TiO_2 photocatalysis

The most used TiO_2 form is anatase, with band gap energy of 3.2 eV. Photon (hv) illumination occurs onto the TiO_2 surface of more than or equal to the BGP follows electron excitation and promotion from the valence band of semiconductor to the conduction band of it.

The degradation capacity of toxins originates 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 isolates these bands by which in the order of electron volts. At the point when a higher energy photon or equivalent 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 at the same time generation of a photogenerated hole (h_{vb}^+) in the valence band and photogenerated electron (e_{cb}^-) in the conduction band. To deliver these two types of carriers, adequate energy must be provided by a photon to promote an electron (e^-) from the valence band to the conduction band, leaving a hole (h+) behind in the valence band. The recombination of holes and electrons is moderate in TiO_2 [9-11].

$$TiO_2 + hv \longrightarrow h^+ + e^-$$

The photo induced hole can oxidize a donor molecule (D) adsorbed on the TiO_2 surface.

$$D + h+ \longrightarrow D^+.$$

The electron in the conduction band can reduce an acceptor molecule (A).

$$A + e- \longrightarrow A^-.$$

The strong oxidation power of the hole enables a one-electron oxidation step with water to produce a hydroxyl radical (OH^o).

$$H_2O + h^+ \longrightarrow OH^o + H^+$$

Here, O_2 which is a electron acceptor reacts with the electron in the conduction band to form a O_2^- . which is a very highly reactive ion [12,13].

$$O_2 + e^- \longrightarrow O_2^-$$

The e^- and h^+ pairs involved in oxidative and reductive reactions are present near the semiconductor surface is shown in figure 2.1.

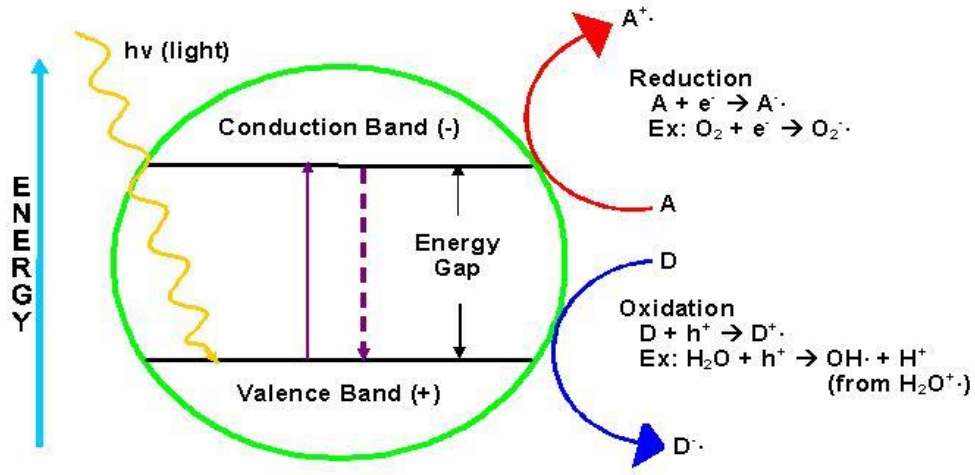

Fig 2.1 Photocatalytic processes on TiO_2 semiconductor[14]

Recent publications proposed that ciprofloxacin and cetirizine were recognized in surface water at more than 1 µg/L. Very high concentrations of ciprofloxacin (14 mg/L) and cetirizine (2.1 mg/L) were found in the discharge of the treatment plants [15].

In the present work we are reporting degradation of cetirizine present in wastewater by photocatalysis by immobilizing TiO_2 on pumic stone which are fixed on glass plates with the help of sand and clay. Pumice stone is a porous material. Immobilization of the photocatalyst was done on a solid support to avoid filtration . Many supports were suggested, i.e. quartz, silica, different kinds of glass, ceramics ,activated carbon , zeolites , glass fibres, stainless steel[16,17].

Chapter 3

REVIEW OF LITERATURE

3.1 Pharmaceuticals in waste water, natural water and surface water

The concern for pharmaceuticals waste as lethal substances in the nature and the need to assess their ecological hazard have extraordinarily expanded since the 21st century. A large portion of urban wastewater is contaminated with therapeutic compounds. The presence of drugs in surface waters, groundwater, and even marine systems has also been confirmed which is due to release of a significant amount of pharma compound. Diclofenac, ibuprofen and amoxicillin are examples of widely utilized pharmaceuticals drugs reported to affect aquatic organisms.

3.2 Environmental impacts of Pharmaceuticals Effluent

India is one of the leading consumers of medicines. A few classes of pharmaceuticals drugs raises serious concern for those produced and consumed in extensive amount. There is a vast possibility of excretion of these pharmaceutical compounds into water cycle. Effluent from pharmaceutical industry, sewage treatment plants, hospitals and homes is dumped into surface and ground water sources causing contamination of drinking water.

3.3 Removal of pharmaceuticals from wastewater using AOPs

Advanced oxidation processes are very convincing technique used for elimination of toxins from wastewater. Advanced existing sewage water treatment technology is deficient for the evacuation of micro pollutants as they are not intended for this particular class of pollutants. These disadvantages of conventional waste water treatment plants for expelling pharmaceuticals raise the critical concern for innovation of technology that can be viably utilized for these compounds. Advanced oxidation processes (AOPs) are considered as appropriate to degrade toxins present in Several AOP techniques includes Ozonation, Photo Fenton, Photocatalysis. The principal of AOPs function is the generation of powerful reactive

free radicals. Hydroxyl radicals are effective in eliminating toxins because they are reactive electrophiles that respond quickly and non-specifically with nearly all electron-rich organic compounds. The remarkable advantage of AOPs over all organic and synthetic procedures is that a lot of hazardous sludge is not produced as in case of activated sludge process and final products are not harmful[18].

A critical review of pharmaceutical waste evacuation by various water treatment processes is investigated and published studies on different pilot- and full-scale WWTPs. Majority of the research is centered on the application of O_3/H_2O_2, O_3, O_3/ OH° and O_3/activated carbon systems for the removal of pharmaceuticals waste from wastewater. In some cases, the removal efficiencies obtained from direct ozonation were low which is increased up to 100% when the ozonation was carried out in the presence of H_2O_2 [19] .

Pharmaceutical micro pollutants present in wastewater lead to a major concern. Medical substances have been identified in samples originating from antibiotics in feed additives and in ground water samples originating from spills [20].

A study based on the treatment of NSAIDs using TiO_2 as a photocatalyst. TiO_2 photocatalysis is a efficient 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.. Therefore, to improve the solar efficacy of wide band gap of semiconductors modified nano material should be used [21].A literature review some important therapeutic compound for photocatalytic degradation of pharmaceutical compounds is shown in table 2.1.

Table 2.1: Literature reviewed for photocatalytic degradation of pharmaceutical compounds[22-26]

Therapeutic Compound	Treatment	Water Matrix	Experimental Conditions	References
Amoxicillin	PC	UV lamp(6W, 365mm)	At lower pH with addition of H_2O_2 and TiO_2 dose of 0.1 g/*l* led to complete degradation.	Elmolla & Chaudhuri (2010)
Paracetamol	PC and DP	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	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)
Carbamazepine	PC	Solar simulator Xe short arc lamp (1000 W)	Degradation of carbamazepine was faster by using TiO2 as a catalyst due to higher adsorption.	Doll & Frimmel (2005)
Carbamazepine and ibuprofen	PC	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 TiO2 catalyst loading. Solar and UV-A photocatalysis appeared to be effective for carbamazepine degradation.	Achilleos et al. (2010)

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 cetirizine in presence of UV light.
2. No study was reported for the photocatalytic degradation of cetirizine using immobilized photocatalyst.

OBJECTIVES

Following objective has been proposed:

1. Photocatalytic degradation of the drug cetirizine 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 cetirizine.
3. To study the photocatalytic degradation of cetirizine using immobilized TiO_2 photocatalyst.

Chapter 4

Materials and Methods

The materials used and methods depict for carrying out the pharmaceutical wastewater treatment is discussed here 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 the procedure followed to carry out the various experiments have been given.

4.1 Materials

4.1.1 Pharmaceutical drug

a) Cetirizine 10mg tablet (Okacet from Cipla) having IUPAC Name 2-[2-[4-[(4-chlorophenyl)-phenylmethyl]piperazin-1-yl]ethoxy]acetic acid shown in Fig4.1 and molecular formula $C_{21}H_{25}ClN_2O_3$ is a widely utilized second-generation histamine H1 antagonist is brought from local market that is utilized for the treatment of allergic rhinitis, chronic urticaria and pollen-induced asthma. Cetirizine has been identified in ground wastewater and surface water which leads to harmful effects on ecosystem hence it has to be completely eliminated from environment. There is no data available on degradation of cetirizine by immobilize immobilized photocatalyst [27].

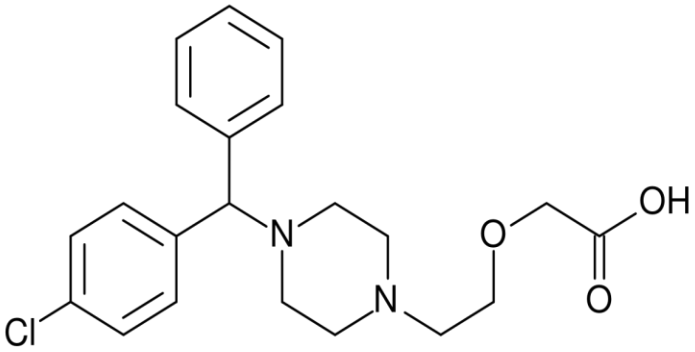

Fig4.1:Chemical Structure of Cetirizine

4.1.2 Catalysts used

AEROXIDE TiO_2 P25 was obtained from Evonik Degussa Corporation, USA. TiO_2 P25 is used as a catalyst which is a fluffy white powder having surface area 50±15 m^2/g. The average particle size of TiO_2 is 30 nm.

4.1.3 Reagents

Hydrochloric acid (HCL) and sodium hydroxide (NaOH) 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 for sample preparation.

4.2 Equipment and instruments

4.2.1 Magnetic stirrer

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

4.2.2 pH meter

The pH of the pharmaceutical drug samples used for carrying out photocatalytic degradation was changed by adding HCL or NaOH (0.1N) solutions and was measured by using Thermo Scientific Orion Star Series pH Meter shown in Fig 4.2.

Fig 4.2:Set up of pH meter

4.2.3 Syringe filter and syringe

A syringe filter generally consists of a plastic housing with a film which serves as a filter. It is also known as wheel filter has a wheel-like shape is a single-use filter cartridge used by attaching a syringe at the one end as shown in Fig 4.3 The syringe contains the solution sample which is to be filtered for the UV analysis.

Fig 4.3: Syringe filter

4.2.4 UV-VIS spectrophotometer

The stock solution was scanned between 200-400 nm wave length to found λ_{max} of wastewater solution using water as blank. Cetirizine showed absorption maxima at 232 nm which is used to measured absorbance of different solutions of different concentrations for plotting calibration curve. For measuring absorbance of the pharmaceutical wastewater 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 4.4. The photocatalytic degradation studies were carried out 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 200 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 as shown in Fig 4.4 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 4.4: Experimental Setup for slurry pond reactor

4.2.6 Fixed bed reactor

A schematic representation of lab scale set up for fixed bed reactor having dimensions (20cm×15cm×5cm) (l×b×h) as shown in Fig4.5 . The photocatalytic degradation studies were carried out using fixed bed reactor. The solution of known concentration was transferred to the reactor with the help of pump. The flow rate was adjusted to ml/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. Glass strips coated with cement on which pumic stone pellets were fixed which are coat with TiO_2 were put inside the reactor as shown in Fig 4.5 and the reaction was started.

Fig 4.5: Experimental setup for Fixed bed treatment

4.3 Experimental procedure

1. The stock solution of cetirizine(40ppm) was prepared by dissolving 4 tablet of cetirizine (10mg) in 1000 ml distilled water using 1L volumetric flask. Stir and sonicate the solution for 30 mins for proper mixing.

2. The stock solution was scanned between 200-400 nm wavelength for checking out λ_{max} of cetirizine which was showed at 232 nm.

3. From the stock solution of cetirizine (40ppm) various concentrations of drug from 5- 30 ppm were prepared by transferring aliquots of stock solution to volumetric flasks of 10 mL and made upto the mark. All the samples are scanned to get different absorptions at different concentrations at absorption max 232 nm.

4. To get the relationship between concentration and absorbance of the wastewater compound, a calibration curve is made. The absorbance is plotted against known concentration of the calibration samples as shown in Fig 5.1.

4.3.1 Procedure used for photocatalytic degradation experiments using shallow pond slurry reactor under UV light for cetirizine is as follow

1. Take desired amount of wastewater solution from the stock solution according to required concentrations(5ppm,15ppm and 25ppm) in the shallow pond reactor and add the desired amount of the TiO_2 catalyst to this solution.
2. Then check the pH of the solution using Thermo Scientific Orion Star Series Meter and change the pH by the addition of HCL or NaOH.
3. The reactor is placed on the magnetic stirrer and magnetic bead is put in the solution for proper stirring.
4. UV lights are switched on. The door of the UV chamber is closed so that no UV rays come out and affect us.
5. After every 30 minutes, take 5ml sample from the reactor with the help of syringe or micropipette
6. The photocatalysis is done for next 420 minutes.
7. To filter the suspended TiO_2 particles from the pharmaceutical drug sample a syringe filter is used.
8. A computer based UV-Vis spectrophotometer was used for determination of absorbance 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 auto zero is done.
d)After auto zeroing, one cuvette is filled with the reference compound (distilled water) and the other one with the samples one by one whose absorbance has to be measured at λ_{max}.

4.3.2 Procedure used for photocatalytic degradation experiments using fixed bed reactor under UV light for cetirizine is as follow

1. The treatment is also carried out on fixed bed reactor at optimization condition obtained from RMS. The photocatalysis is done for 10 hrs on fixed mode.
2. After every 60 minutes, take 5ml sample for checking % degradation by UV-Vis spectrophotometer.

Now, we know variation of absorbance of samples with time which 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 doses.

4.3.3 Procedure for immobilization

The general procedure for immobilization is as follow:

1. 6 gm of TiO_2 was dissolved in 400ml of distilled water with continuous stirring followed by sonication, until TiO_2 dispersed properly.
2. Immobilization of TiO_2 was done on pumic stone. Pumic stone pellets coated with TiO_2 were fixed on glass by using Portland cement and sand brought from local market.
3. The glass strips on which pumic stone is fixed were coated with TiO_2 slurry and allowed to dry in oven at 100^0C.
4. Dry strips were calcined for 2 hr at 400^0C.
5. It was repeated for 3 times to get uniform coating of TiO_2 on the pumic stones.

4.4 Optimization

Photocatalytic treatment of pharmaceuticals wastewater is a very complicated treatment. This complexicity is caused by 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. As the photocatalytic treatment of wastewater relies upon number of variables .So, it is important to study about the associated. Information gathered from the analyses have been utilized for optimization which was done by Response Surface Methodology (RSM).

The Box-Behnken design is an independent quadratic design that does not contain an embedded fractional factorial design. In Box-Behnken design the treated combinations are at the midpoints of edges of the process space and at the center. These designs are rotatable and require 3 levels of each factor[28-29].

Optimization by Box-Behnken Design (BBD)

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

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

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

$$Y = S_0 + \sum_{i=1}^{k} S_i X_i + \sum_{i=1}^{k} S_{ii} X_i^2 + \sum \sum_{i<j} X_i Y_i + K_t$$

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 for wastewater treatment, the Statistical Design-Expert software version 6.06 (STAT-EASE Inc., Minneapolis, US) was used.

Chapter 5

RESULTS AND DISCUSSIONS

In this chapter we have studied the effect of operating parameters on the % degradation of pharmaceutical compound cetirizine by the photocatalysis process. The experimental results and their interpretation regarding pharmaceutical compound cetirizine degradation using photocatalysis have been discussed in detail.

5.1Calibration Curve

The complete wavelength scan of compound cetirizine was done on UV-Vis spectrophotometer and maximum absorbance was observed at 232nm. Standard curve was obtained by plotting the graph between absorbance and concentration of cetirizine as shown in Fig 5.1.

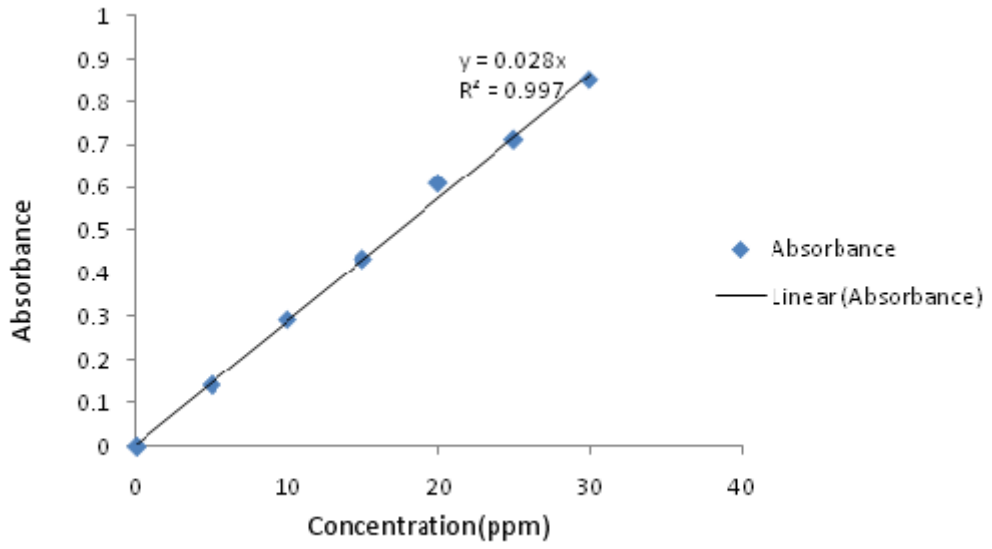

Fig 5.1: **Calibration curve for cetirizine**

5.2 Degradation of cetirizine wastewater by photocatalysis

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

5.3 Response Surface Methodology (RSM)

1) Box- Behnken Design (BBD)

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

Table 5.1: Range of variables and coded levels

Variables	-1	0	1
TiO_2 dose (g/*l*)	0.5	1.5	2.5
pH	3	7	11
Cetirizine conc. (ppm)	5	15	25
Time(min.)	30	225	420

A full factorial design has been used to study the photocatalytic degradation of cetirizine and is shown in Table5.2. The total of 25 experiments was suggested by BBD to optimize the process parameters such as TiO_2 dose, pH, concentration and time for % degradation of cetirizine.

Table 5.2: Full factorial BBD matrix used and simulated data response

Std	pH	TiO_2 Dose	Time(min.)	Ctz Conc.(ppm)	%Degradation
1	7	0.5	225	25	20.25
2	7	1.5	225	15	38.94
3	7	1.5	225	15	38.94
4	7	0.5	225	5	9.21
5	11	1.5	225	25	6.78
6	3	0.5	225	15	34.79
7	11	1.5	30	15	1.70
8	7	1.5	30	5	0.01
9	3	1.5	225	5	34.32
10	7	2.5	225	25	38.95
11	7	1.5	30	25	1.96
12	11	1.5	420	15	7.65
13	11	2.5	225	15	6.78
14	7	2.5	225	5	24.87
15	7	1.5	225	15	38.94
16	11	1.5	225	5	21.58
17	7	0.5	30	15	2.07
18	7	0.5	420	15	25.11
19	7	1.5	420	5	28.36
20	7	2.5	420	15	65.20
21	3	1.5	420	15	75.66
22	3	1.5	225	25	48.80
23	7	1.5	420	25	53.44
24	7	1.5	225	15	38.94
25	7	2.5	30	15	0.01

2) Statistical analysis

The % degradation of photocatalysis of cetirizine was optimize 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 cetirizine. was found to be less than 0.0001 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 cetirizine. Sequential model sum of squares showed that quadratic model was best fit model for experimental data for % degradation of cetirizine. Cubic model was found to be aliased for degradation of cetirizine.

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

Source	Sum of Squares	DF	Mean Square	F Value	Prob>F	
Mean	22584.10	1	22584.10			
Linear	11001.26	4	2750.31	13.68	< 0.0001	
2FI	2887.56	6	481.26	4.47	0.0061	
Quadratic	1264.24	4	316.06	6.57	0.0034	Suggested
Cubic	528.20	8	66.02	2.72	0.1196	Aliased
Residual	145.61	6	24.27			
Total	38410.98	29	1324.52			

The Prob > F value was 0.0001, which indicates that quadratic model is significant. The coefficient of determination is 0.95 for quadratic model. The difference between predicted values and observed values dividing by standard error of the residual has close relation with % Normal probability. This shows a proficient correlation between the predicted and observed values as shown in Fig 5.2. The predicted values were closer to the actual values.

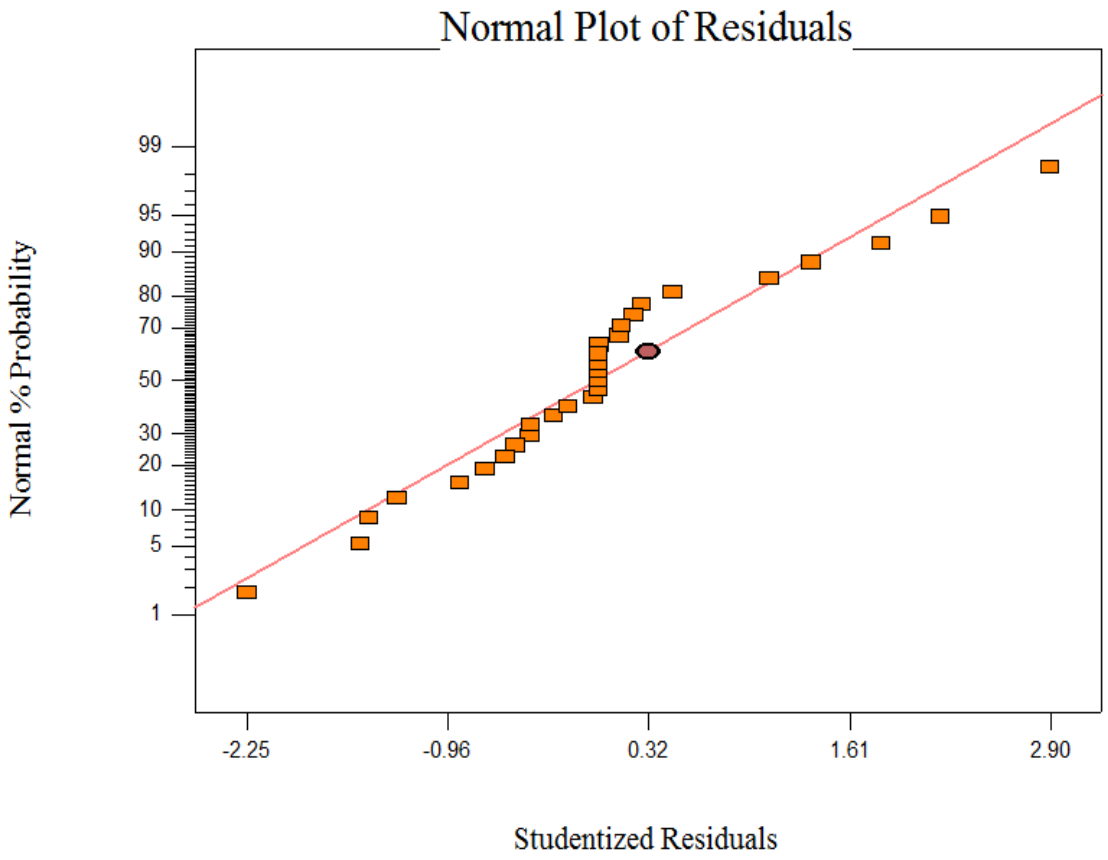

Fig 5.2: Residual plot for photocatalysis of % degradation of cetirizine

The ANOVA (analysis of variance) shows the model F-value for %degradation of cetirizine is as shown in Table 5.4. This showed that model considered is significant for % degradation of cetirizine. For model terms to be significant, "prob>F" values should be less than "prob>F" values larger than indicates that model term are insignificant. From ANOVA it is clear that the time and TiO_2 dose are highly significant terms for %degradation of cetirizine.

Table 5.4: Analysis of variance suggested by BBD for the % degradation of cetirizine

	% degradation of cetirizine				
Source	Sum of Squares	DF	Mean Square	F Value	Prob>F
Model	15153.06	14	1082.36	22.49	< 0.0001 significant
pH	4440.17	1	4440.17	92.26	<0.000
TiO_2 Dose	1264.38	1	1264.38	26.27	0.0002
Time	5072.81	1	5072.81	105.40	< 0.0001
Ctz Conc.	223.90	1	223.90	4.65	0.0489
pH^2	24.26	1	24.26	0.50	0.4894
$TiO2 \times Dose^2$	86.68	1	86.68	1.80	0.2010
$Time^2$	943.95	1	943.95	19.61	0.0006
Ctz $Conc^2$	526.79	1	526.79	10.95	0.0052
pH×Tio2 Dose	978.75	1	978.75	20.34	0.0005
pH×Time	1114.22	1	1114.22	23.15	0.0003
pH×Ctz Conc.	214.34	1	214.34	4.45	0.0533
TiO_2 Dose×Time	444.22	1	444.22	9.23	0.0089
Time×Ctz Conc.	2.31	1	2.31	0.048	0.8297
Time×Ctz Conc.	133.71	1	133.71	2.78	0.1178
Residual	673.81	14	48.13		
Lack of Fit	673.81	10	67.38		
Pure Error	0.00	4	0.000		
Cor Total	15826.87	28			

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

To study the effect of parameters i.e. TiO_2 dose, pH, concentration of compound and time on % degradation of cetirizine(response) for photocatalysis of pharmaceutical compound, the three dimension response surface graph were considered for present study. We can examine from the Fig 5.3 (a),(b) and (c).

From Fig. 5.3(a) it was observed that with the increase in pH at all the concentration of TiO_2 dose % degradation is decreasing. The % degradation is maximum at pH 3.35 with higher concentration of TiO_2.

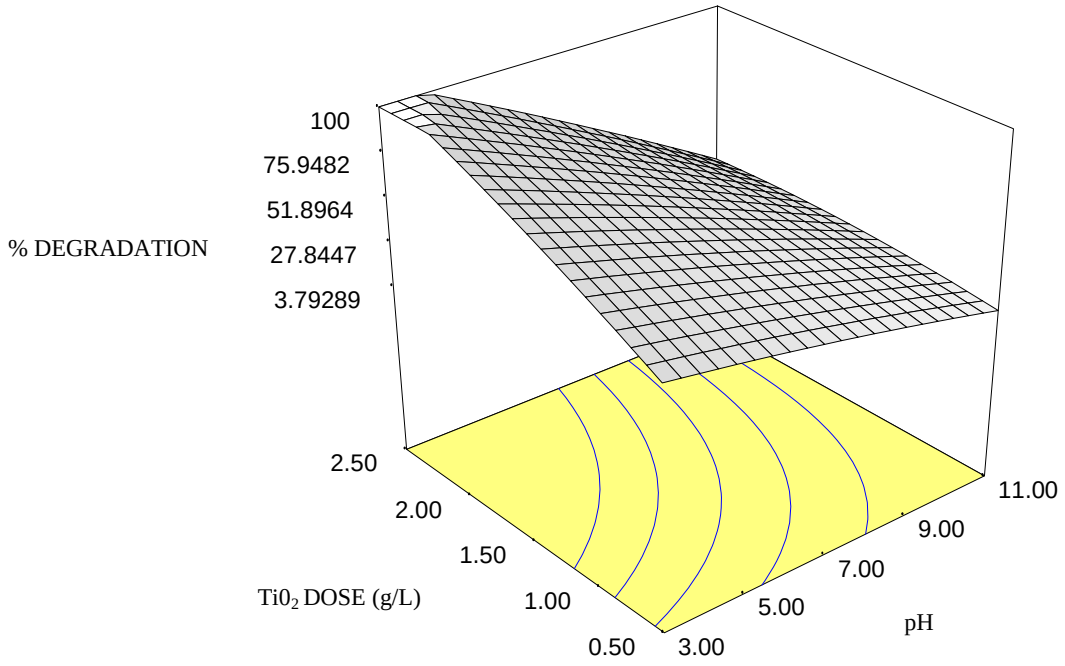

Fig5.3: (a) %degradation 3-D response surface graph between pH and TiO_2 dose and pH

The 3D plot Fig. 5.3 (b) shows that the effect of pH and time on the % degradation. It has been clearly seen that at all the pH values the % degradation is increased with increase in time but at lower range of pH with the increase in time the % degradation is maximum.

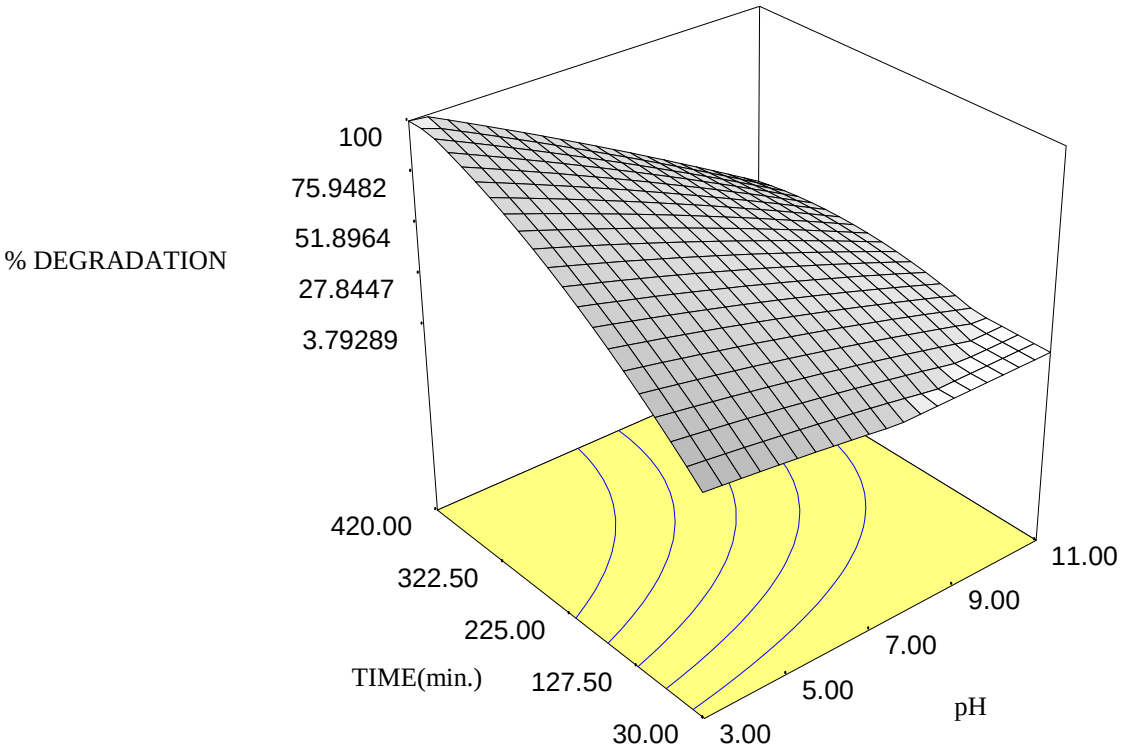

Fig5.3:(b) % degradation of cetirizine 3D response surface graph between pH and time

In Fig 5.3(c) the effect of time and TiO_2 dose on % degradation is studied. The % degradation at all the TiO_2 dose with increase in time also increase. But at the TiO_2 dose 2.32g/*l* with the increase in time degradation is maximum.

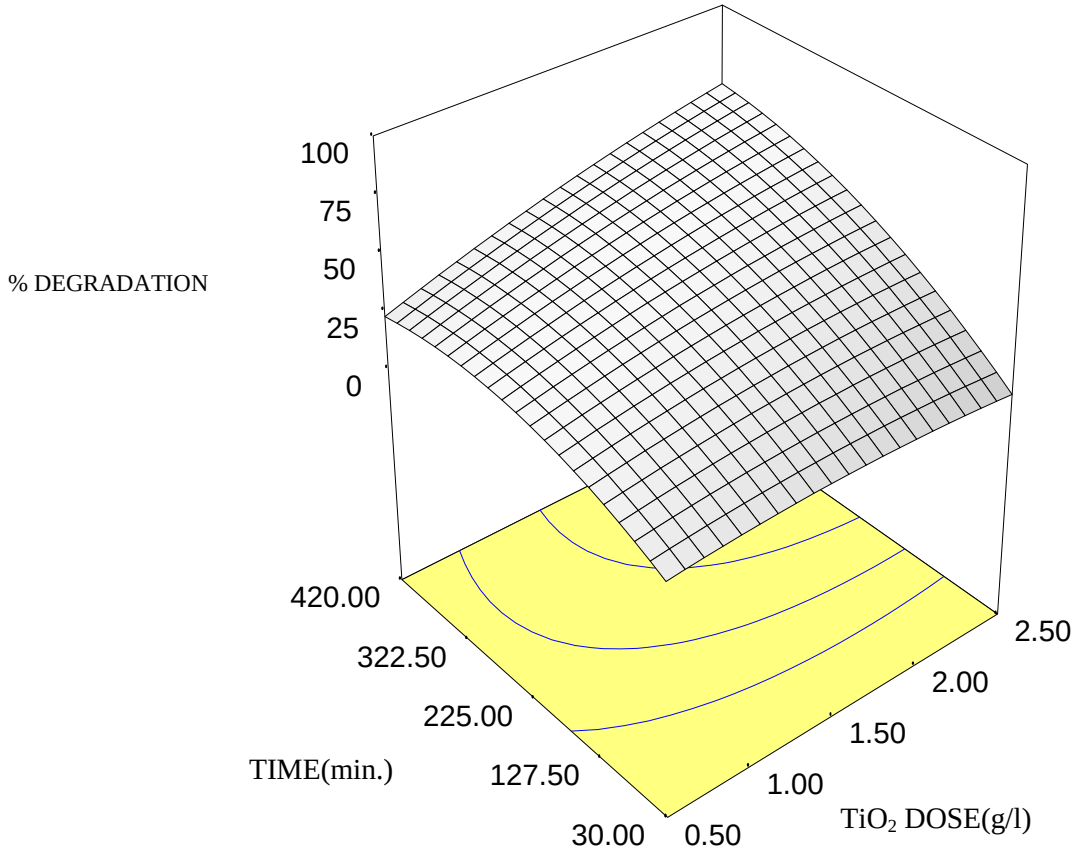

Fig5.3: (c) % degradation of cetirizine 3-D response surface graph between TiO_2 dose and time

Fig 5.3(a),(b),(c) concluded that, Photocatalytic degradation of a compound is done by the $OH^{\cdot}$ attack which 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 participates in the degradation of the cetirizine. From regression analysis, it was concluded that in acidic condition at the higher dose of TiO_2 % degradation of cetirizine was more. The catalyst behavior can be explained by TiO_2 surface charge density.

4) Optimization analysis

Photocatalysis of cetirizine was optimized by BBD as %degradation of cetirizine 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

Factor	Level	Low Level	High Level	Std. Deviation
pH	7.00	3.00	11.00	0.000
TIO_2 DOSE	1.50	0.50	2.50	0.000
TIME	225.00	30.00	420.00	0.000
CTZ CONC	15.00	5.00	5.00	0.000

In this study, % degradation of cetirizine was optimized in terms of maximization using BBD. The values of optimum parameters were found to be TiO_2 dose= 2.32 g/*l*, t= 410 min and pH=3.35, desirability of D = 0.99 was produced. At this optimum condition, the % degradation of cetirizine suggested by BBD was to be % for cetirizine concentration 15ppm as shown in Table 5.6.

Table 5.6 : Optimum conditions for photocatalytic degradation of cetirizine

Variable	Optimum values
PH	3.35
Time(t)	410 mins
TiO2 Dose	2.32g/l

5) Confirmation results

Optimum condition for photocatalytic treatment of pharmaceutical drug was verified experimentally. Experiment was run for 410 mins at pH 3.35 with TiO_2 dose 2.32 g/*l*. Hence, the predictions agreed well with the experimental and optimization results by RSM.

6) Fixed bed treatment

The main advantage for developing this method is to get rid of difficult and costly step of filtration and recycle the catalyst. For fixed bed treatment the experiment was run on recycled for 10 hours. The experiments was carried out at different flow rates less the flow rate more will be % degradation and vice-versa. The experiment was repeated 3 times for three different flow rate 700ml/hr, 480ml/hr and 228ml/hr. The results obtained are shown in graph in Fig 5.4 which clearly shows that at lower flow rate the % degradation was maximum .Because at lower flow rate wastewater is getting more time to stay in reactor in contact with photocatalyst due to which degradation occurs.

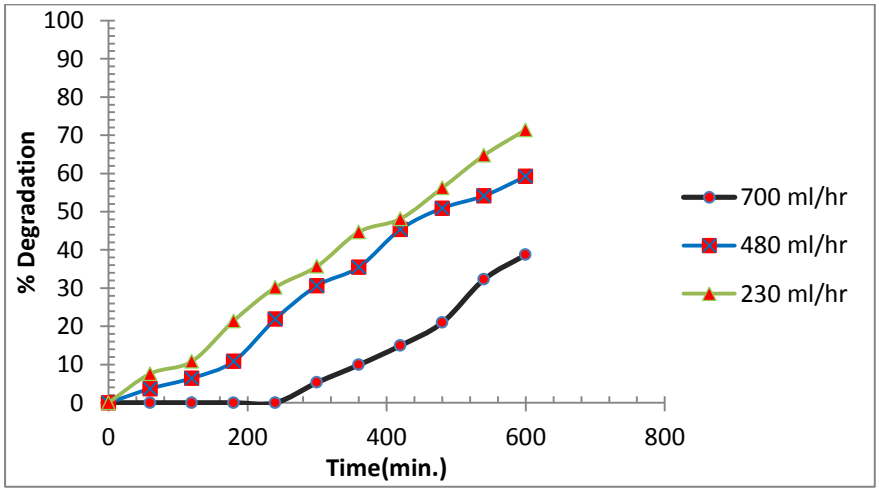

Fig5.4:Graph for three different flow rates for fixed bed treatment

7) Kinetic study

The kinetics study of cetirizine wastewater was studied for photocatalytic treatment process at optimum conditions(TiO_2 dose = 2.32g/*l*, pH = 3.35, t= 410 min) obtained from RSM. For the experimental results of photocatalytic treatment of cetirizine first order model was fitted as shown in Fig 5.5 .

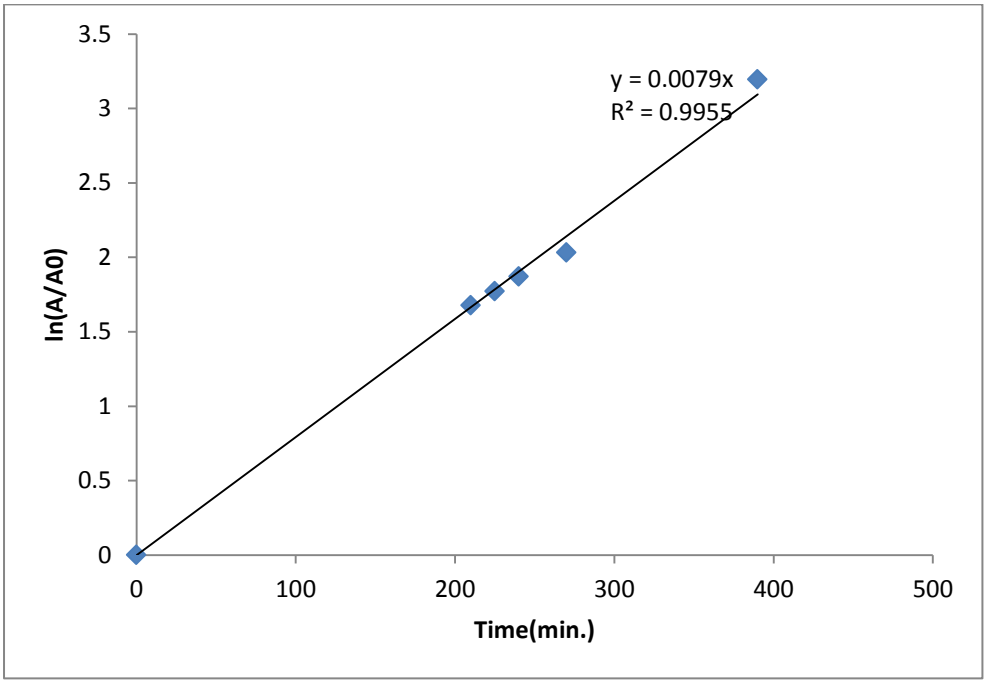

Fig 5.5. Kinetic study of photocatalytic treatment of cetirizine followed by first order model

According to the first order rate equation

$$\text{Rate} = -\frac{d[A]}{dT} = k\,[\text{A}]$$

Here "Rate" is the reaction rate (molar/time) and *k* is the coefficient of reaction rate (1/time)

Integrate both sides of the above rate equation

$$\int_{[A]_\circ}^{[A]} \frac{d[A]}{[A]} = - \int_{t_\circ}^{t} k dt$$

Upon integration

$$\ln[A] - \ln[A]_\circ = -kt$$

This can be arranged into y = m + x

$$\ln[A] = -kt + \ln[A]_\circ$$

The equation is a straight line with slope m

$$mx = -kt$$

and y-intercept b:

$$b = \ln[A]_\circ$$

So,

$$\ln\left(\frac{[A]_t}{[A]_\circ}\right) = - kt$$

The R^2 value for kinetic study was 0.995 with rate constant value $k = 0.007 min^{-1}$

CONCLUSION

Heterogeneous photocatalysis process is a very efficient method for reducing organic or inorganic pollutants present in wastewater. This process has proved its superiority to other conventional methods for micro pollutants. It leads to complete degradation of harmful contaminants. In the present study the heterogeneous photocatalytic degradation for the pharmaceutical compound cetirizine wastewater with UV/TiO_2 was assessed. Pharmaceutical compound cetirizine has been successfully degraded in the presence of TiO_2 photocatalyst. For optimization of responses BBD was used. The values of R^2 for BBD was 0.95, which indicated that model was significant. It was examined that photocatalytic process was an efficient process for degradation of cetirizine at lower pH and higher TiO_2 dose with the increase in time. The % degradation of cetirizine was optimized. The optimum conditions of parameters were found to be TiO_2 dose= 2.32g/*l*, t= 410 min and pH=3.35, which showed an overall desirability of 1.000. At optimum condition the % degradation of cetirizine suggested by BBD was 100%. To verify the suggested response of experiments conformational experiment was performed. Experimentally % degradation of cetirizine at optimum conditions was found to be 98.38 % for slurry mode reactor and 71.4% for fixed bed mode reactor. The kinetic study shows that the degradation rate is followed by first order kinetics model having rate constant value k = 0.007 min^{-1}.

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Pooja Photocatalytic degradation

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