SLURRY AND FIXED BED PHOTO CATALYTIC DEGRADATION OF HERBICIDE 4-CHLORO PHENOXY ACETIC ACID USING DOPED/UNDOPED CATALYST

A Dissertation

Submitted in partial fulfillment of the requirement

For the award of degree of

Masters in Technology

in

ENVIRONMENTAL SCIENCE & TECHNOLOGY

Submitted by

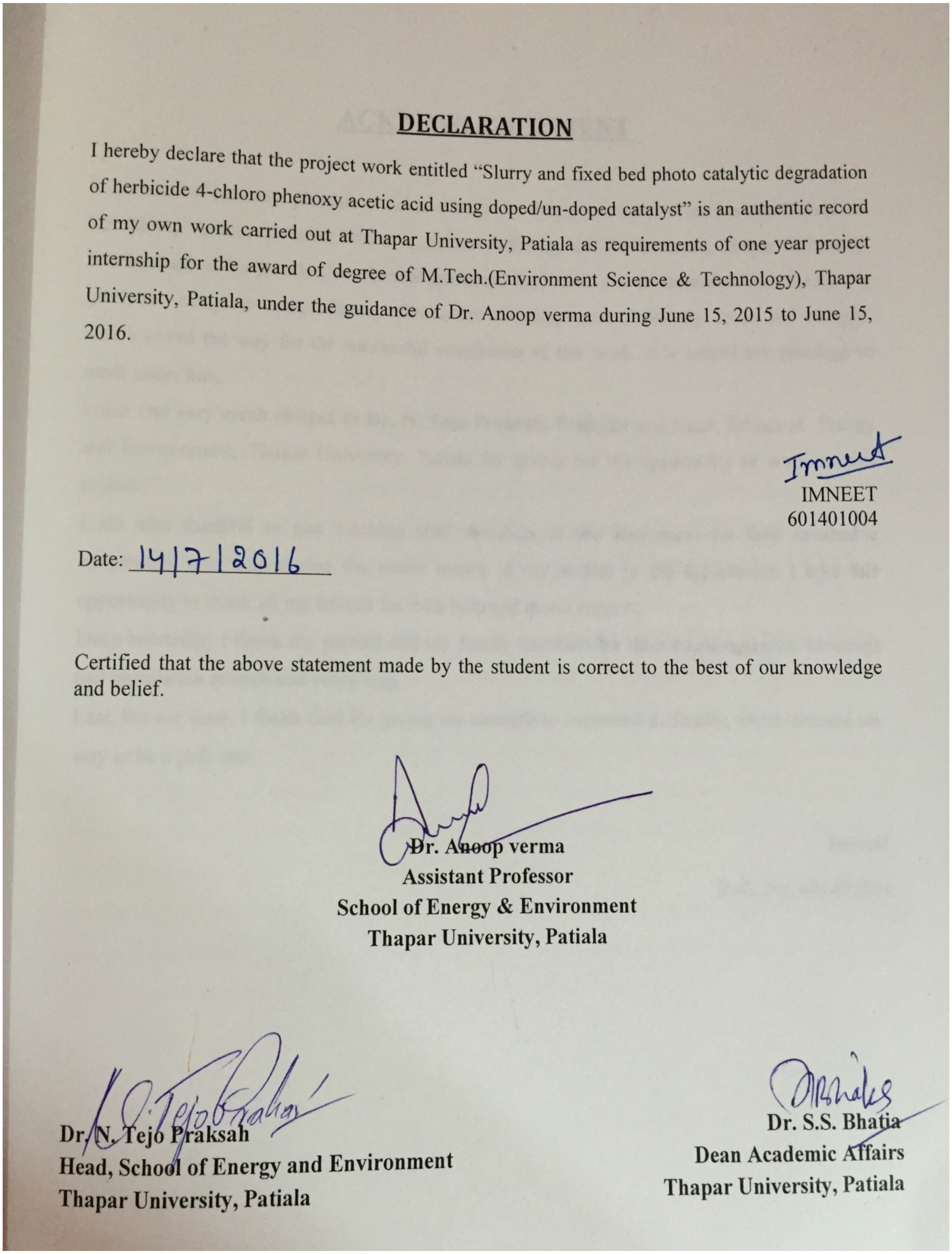
Imneet

Roll No: 601401004

Under the Guidance of

Dr. Anoop Kumar
Assistant Professor
School of Energy & Environment
Thapar University, Patiala

SCHOOL OF ENERGY AND ENVIRONMENT
THAPAR UNIVERSITY, PATIALA
(Declared as Deemed-to-be-University u/s 3 of the UGC Act, 1956)
July 2016



DECLARATION

I hereby declare that the project work entitled "Slurry and fixed bed photo catalytic degradation of herbicide 4-chloro phenoxy acetic acid using doped/un-doped catalyst" is an authentic record of my own work carried out at Thapar University, Patiala as requirements of one year project internship for the award of degree of M.Tech.(Environment Science & Technology), Thapar University, Patiala, under the guidance of Dr. Anoop verma during June 15, 2015 to June 15, 2016.

Imneet

IMNEET
601401004

Date: 14/7/2016

Certified that the above statement made by the student is correct to the best of our knowledge and belief.

Dr. Anoop verma
Assistant Professor
School of Energy & Environment
Thapar University, Patiala

Dr. N. Tejo Praksah
Head, School of Energy and Environment
Thapar University, Patiala

Dr. S.S. Bhatia
Dean Academic Affairs
Thapar University, Patiala

ACKNOWLEDGEMENT

It is matter of immense pleasure to acknowledge my debt to my revered teacher and Supervisor **Dr. Anoop verma,** Assistant Professor, School of Energy and Environment, Thapar University. It is because of his priceless intellectual guidance, innovative and constructive ideas for having given me complete independence, affectionate encouragement to put my desire and thought, which paved the way for the successful completion of this work. It is indeed my privilege to work under him.

I also feel very much obliged to **Dr. N. Tejo Praksah,** Professor and Head, School of Energy and Environment, Thapar University, Patiala for giving me the opportunity to work on this project.

I am also thankful to non teaching staff members of the department for their invaluable cooperation and help during the entire tenure of my studies in the department. I take this opportunity to thank all my friends for their help and moral support.

Deep heartedly, I thank my parents and my family members for their encouragement, blessings and motivation at each and every step.

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

Imneet

Roll. No. 601401004

ABSTRACT

The introduction of chlorinated aromatic compounds as herbicides into the environment is a matter of great concern due to their toxicity. The chemical resistance of these compounds makes their removal from contaminated waters a difficult task. In this regard, photo catalytic reactions provide an auspicious solution to this problem. The present study focuses on the degradation of a herbicide 4-chlorophenxyacetic acid in a shallow pond slurry reactor through heterogeneous photocatalysis using TiO_2 as a photo catalyst in suspended as well as supported form. The influence of various parameters like dose of photo catalyst, oxidant, A/V ratio of the reactor, pH, and UV intensity have been studied under UV-A (365 nm) irradiations. The degradation rate was found to follow the pseudo first order rate kinetics. The optimized conditions for better degradation in case of slurry photocatalysis were TiO_2 dose 0.625 g L^{-1}, oxidant dose 0.125mL per 200mL, UV intensity 25 Wm^{-2}. All experiments were conducted at solution's natural pH i.e. 3.5. For fixed-bed studies, TiO_2 coated clay beads were used and 92% degradation of 4-CPA was achieved after 3 h of treatment using these catalyst immobilized beads. A significant amount of degradation was achieved when experiments were performed in natural solar light for the degradation of concerned pollutant under optimized conditions. Efforts were also made to dope the catalyst with certain metals like iron and copper. The degradation rate for 4-CPA was fastened and enhanced when doped catalyst was used as around 94% degradation occurred while 85% degradation was attained in case of un-doped catalyst after three hours of photo catalytic treatment. The mineralization of 4-CPA was confirmed by reduction in COD (85.7%) along with the generation of chloride ions (75%), after 2 h of irradiation as well as elimination of the parent compound peak in HPLC chromatograms . Scale–up of the studied photo-oxidation process can lead to its feasibility at pilot-scale in near future for the treatment and removal of recalcitrant compounds like 4-chlorophenxyacetic acid present in water bodies.

TABLE OF CONTENTS

LIST OF FIGURES

Chapter 1

Introduction

The economy in developing countries like India mainly depends upon the development of agriculture sector so as to promote self sufficiency in food, increase gross domestic productions, to increase and generate employment. To achieve these targets, farmers are encouraged to use improved seeds, fertilizers and pesticides. But the exposure of the pesticide both occupationally and environmentally causes a range of human health problems because pesticides are very toxic in nature **(Babu *et al*., 2011)**. The most important portion of contamination due to pesticide /agrochemical wastewater is observed in agricultural areas and in surface waters .The major pollution of the pesticide wastewater is released from pesticide/ agrochemical manufacturing industry wastewater **(Misra *et al*., 2013)**.

Chlorinated aromatic compounds also come under noxious chemicals that usually enter the environment as fungicides and herbicides. Chlorophenoxy herbicides are extensively employed for controlling weed over cereal crops, lawns and grasslands. Generally, 4-chlorophenoxyacetic acid which is used as a model pollutant in our proposed study comes under chlorophenoxy herbicides and is utilized for improving setting of fruits on tomatoes, repressing formation of sprouts in mung beans and for thinning of fruits in peaches. These compounds are chemically resistant, non-biodegradable and are potentially toxic for humans and animals (**Hoar *et al*., 1986)**. Moreover, these compounds are classified as class II or III (moderately toxic) by WHO (World Health Organization). They are used for agricultural and non-agricultural purposes thereby producing rinsate, wastes leading to the contamination of soil at huge number of sites. They have been detected in natural waters up to the concentration of 10 μgL^{-1} in surface and ground waters **(Aaron *et al*., 2001)**. For this purpose, there is need of an hour to develop environment friendly methods having sufficient oxidizing capacity to decompose these types of compounds in wastewater thus preventing their persistence in environment.

The positive aspect of using pesticides includes enhanced crop/food productivity and drastic reduction of vector-borne diseases. However, their unregulated and indiscriminate use has raised serious concerns about the entire environment (fig 1.1) in general and the health of humans, birds and animals in particular (Agrawal *et al*; 2010).

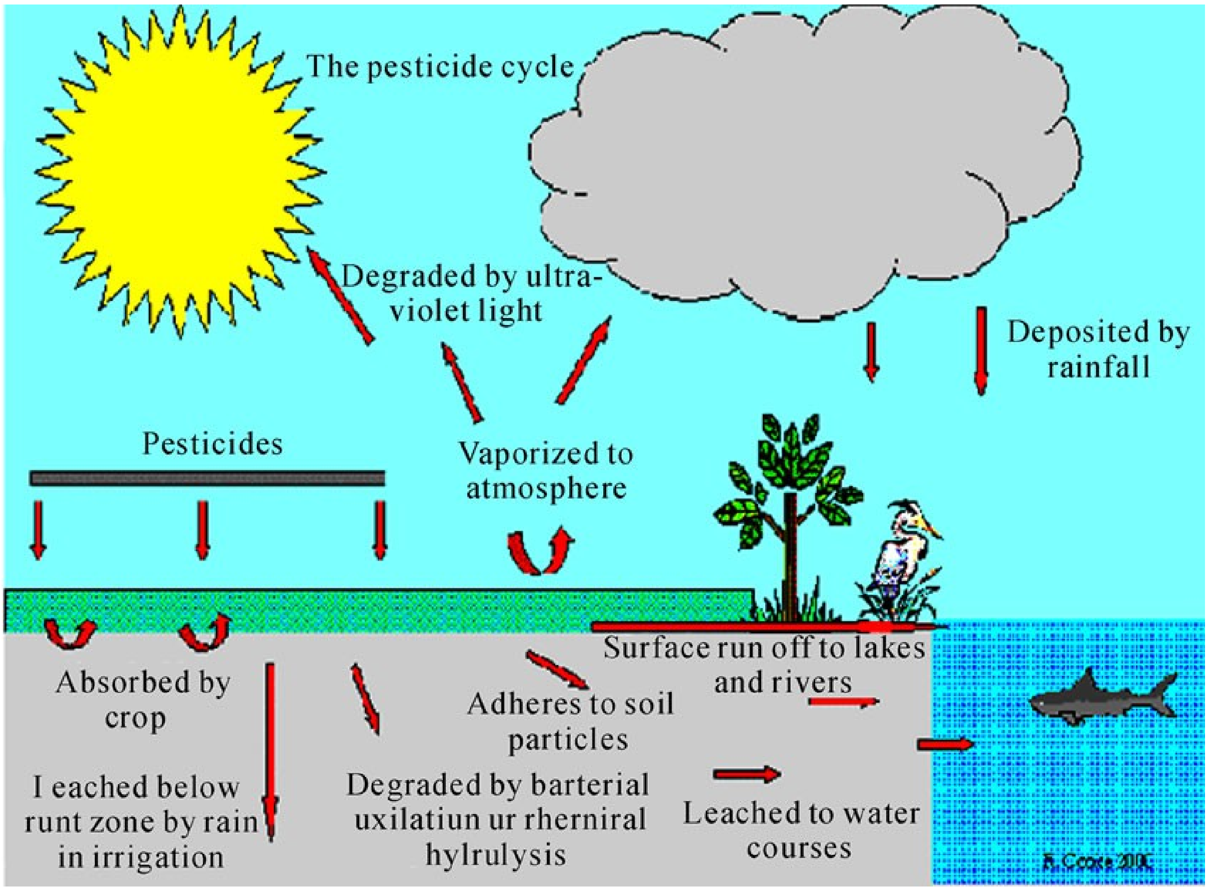


Fig 1.1 Fate of pesticides in environment

Photo catalytic degradation is one of the most prominent techniques among advanced oxidation processes for treating wastewater contaminated with such types of bio-recalcitrant compounds. Heterogeneous photocatalysis is one of the widely used processes for the removal of persistent organic contaminants like pesticides **(Burrows *et al.*, 2002; Kaneko and Okura, 2003; Konstaninou and Albanis, 2003)**. These processes have been focused in recent years due to the incapability and inefficiency of the conventional treatment technologies including biological treatment, chemical oxidation, carbon adsorption, etc to degrade the organic pollutants completely. The main drawbacks of these conventional methods are the slow rates of reaction, disposal problem for sludge and moreover, these methods are incapable of mineralizing the organic compounds thereby leading to an immediate requirement of some effective advanced treatment techniques like photocatalysis. Various catalysts like CdS **(Davis *et al.*, 1990)**, ZnS **(Yin *et al.*, 2001)**, ZrO_2, SnO_2 and WO_3 **(Wissiak *et al.*, 2000; Galindo *et al.*, 2001)**, ZnO **(Yin *et al.*, 2001)**, TiO_2 **(Sclafani *et al.*, 1990; Toor *et al.*, 2006; Verma *et al.*, 2012)** have been used and studied in photo catalytic degradation processes. But TiO_2 is one of the most commonly used materials due to its stability, cheapness, commercial availability and photo activity.

Vast investigations have already been carried out as well as published in number of research papers on the photo catalytic degradation of numerous types of organic compounds like dyes, nitro phenols, pharmaceuticals, pesticides **(Xu *et al*., 2000; Verma *et al*., 2013, 2014a, b)**. However, use of photo catalytic processes for the degradation of herbicides and pesticides present in wastewater in lower concentrations has received a great attention during the last few years. Semiconductor-mediated photocatalysis is becoming one of the promising environment friendly technologies for treating recalcitrant organic pollutants like herbicides.

The mechanism of TiO_2 photocatalysis (fig. 1.2) is now well established where it shows the generation of hydroxyl radicals ($^{\cdot}OH$) which can degrade large variety of pollutants present in wastewater bodies. The hydroxyl radicals react rapidly and easily with organic molecules which are adsorbed on surface, either by hydrogen atom or electron which results in the degradation of target compound **(Sadik *et al*., 2007)**. The reactions 1-6 describe the complete mechanism of TiO_2 photocatalysis.

(1) $TiO_2 + hv \rightarrow TiO_2\ (e^- + h^+)$

(2) $h^+ + H_2O \rightarrow H^+ + {}^{\cdot}OH$

(3) $h^+ + OH^- \rightarrow {}^{\cdot}OH$

(4) Organics + $^{\cdot}OH$ → Degradation products

(5) $e^- + O_2 \rightarrow {}^{\cdot}O_2$

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

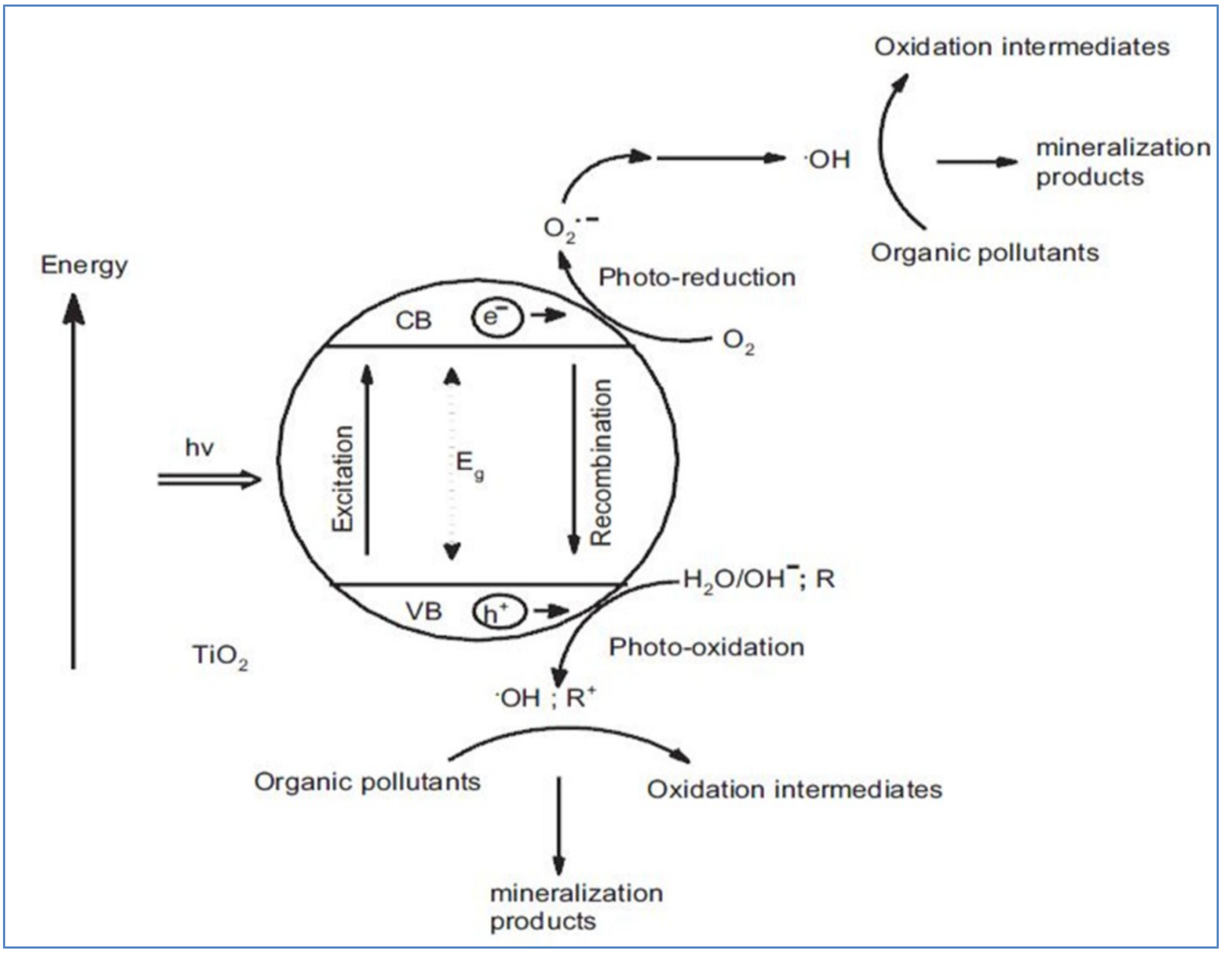


Figure 1.2: Mechanism of TiO_2 photocatalysis.

The separation of catalyst from slurry is always a difficult task to do towards its commercial applications. This problem can be technically solved by Immobilization or on inert support. Studies related to catalyst fixing on supports are cited in literature **(Daneshvar *et al*., 2005, Verma *et al*., 2014c)** although durability, recyclability and cost of the support have not been covered. The present work covers these concerns by coating TiO_2 on inert support materials like clay beads and study them for the degradation of the target compound.

The main disadvantage of immobilization of catalyst is that photo catalytic efficiency gets reduced along with limited mass transfer conditions but metal or metal ion doping increases the photo catalytic efficiency significantly. Metal-doped TiO_2 becomes photoactive in visible light as well by the production of new energy level in the band gap of TiO_2 by divergence of metal nanoparticles in TiO_2 matrix. The detailed procedure is shown in fig 1.3.The main advantage of doping the catalyst with metals is the prevention of electron-hole recombination which results in increasing the photo catalytic efficiency.

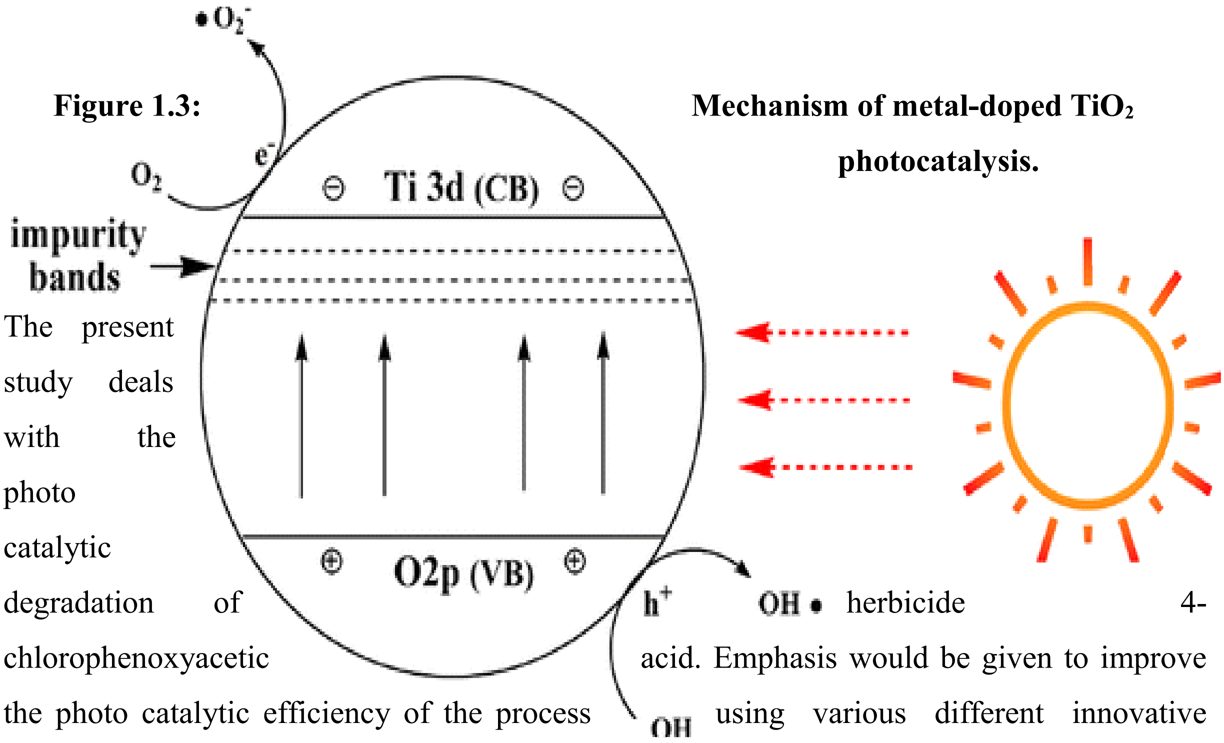


Figure 1.3: **Mechanism of metal-doped TiO_2 photocatalysis.**

The present study deals with the photo catalytic degradation of herbicide 4-chlorophenoxyacetic acid. Emphasis would be given to improve the photo catalytic efficiency of the process using various different innovative trails. Experiments would be performed on suspended TiO_2/modified TiO_2 and efforts would be entertained as well to immobilize both forms of catalyst on some inert support material to overcome the problem of filtration post treatment.

Chapter 2

Literature Review

The pesticide production in India started with the production of Benzene Hexa Chloride (BHC) near Calcutta in 1952 **(Singh *et al.*, 2010)**. Now, India is the second largest producer of pesticides in Asia after China and rank 12th in the world **(Singare and Dhabarde, 2014)**. The worldwide consumption of the pesticide is nearly 2 million tons per year, of which 3.75% is consumed in the India **(Pathak and Dikshit, 2011)**. Over the years herbicides have emerged as an important tool in management of weeds. Herbicides use is increasing throughout the globe due to increasing labor cost, choice of application of herbicides, quick weed control in crop and non-crop areas etc. In recent years, advanced oxidation processes (AOP's) have received increasing attention as they are successful in degradation of bio-resistant and toxic compounds without creating secondary pollution. Photo catalytic degradation is an advanced but non selective oxidation process, which has been successfully used to oxidize many organic pollutants present in aqueous systems **(Ashfaq and Khatoon, 2014)**.

Advanced Oxidation Processes (AOPs)

AOPs are oxidative methods that involve the formation of intermediate radicals, the hydroxyl radicals ($OH^{\bullet}$), which are highly reactive and less selective compared to other oxidants (e.g. chlorine, molecular ozone). Its standard oxidation potential being greater than the conventional oxidants, makes them highly effective in the oxidation of a number of organic compounds **(Hernandez *et al.*, 2002; Bautitz and Nogueira, 2007)**. These radicals are generated from oxidizing agents like ozone or hydrogen peroxide that are generally combined with metallic or semiconductor catalysts and UV radiation. Various techniques like Fenton, photo-Fenton, cavitation, ozonation, photocatalysis, etc. comes under AOPs and they vary only with the source of radicals **(Kim and Ihm, 2010)**.

Heterogeneous Photocatalysis

Photocatalysis is the advancement of a photochemical transformation using a catalyst such as TiO_2 or Fenton's reagent (**Chatterjee and Dasgupta, 2005; Herrmann, 2005;**

Dalrymple ***et al.*****, 2007**). Most of the photo catalysts are semiconductor metal oxides which usually possess a narrow band gap. Radicals that are generated react with impurities in the wastewater and degrade them unselectively (**Lhomme** ***et al.*****, 2008**). Titania is the most widely used heterogeneous photo catalyst which is mainly because of its cost effectiveness, inertness and photostable nature (**Gaya and Abdullah, 2008**). TiO_2 can either be used in slurry form or supported form. The degradation of bipenyls and chlorobiphenyls using TiO_2 photocatalysis in aqueous mode is the first reported study (**Carey** ***et al.*****, 1976**). Since then, the number of publications has grown considerably regarding the removal of micro pollutants through TiO_2 photocatalysis in slurry form (**Doll and Frimmel, 2005a, b, c; Perez-Estrada et al., 2005a**).

Toor ***et al.*****, 2013** carried out research for the photo catalytic degradation of an herbicide, Isoproturon in aqueous solution using TiO_2. The optimum conditions obtained for the better degradation of compound were TiO_2 dose of 0.5 gL^{-1}, pH 5.0, and C_0 25 mgL^{-1}. The mineralization studies were also performed which were confirmed by the reduction in COD (96 %) and TOC (90 %) along with the generation of ammonium ions whereas various intermediates formed were confirmed by the data of HPLC and LC-MS study.

The degradation of herbicide, Paraquat using UV/TiO_2 photocatalysis was investigated by **Leyva** ***et al.*****, 1998**. According to the experimental results, direct photolysis showed slower degradation of Paraquat in the presence of dissolved oxygen. While addition of TiO_2 showed a substantial increase in the initial rate of reaction. Complete photo catalytic degradation occurred after three hours of irradiation at high pH.

Verma ***et al.*****, 2012** investigated the photo catalytic degradation of an insecticide, Chlorpyrifos using TiO_2 in aqueous phase under artificial UV-A and solar light. The optimum operating conditions for better degradation were determined which were obtained as TiO_2 dose 4 gL^{-1}, pH 6.5 and H_2O_2 3 gL^{-1} at which 90 % degradation was achieved. It was observed that better results were obtained under sunlight as compared to artificial UV light. The effect of sonication on TiO_2 slurry for better dispersion of the catalyst particles was also studied.

The sonolytic, sonophotocatalytic as well as photo catalytic degradation of 4-chloro-2-nitrophenol was investigated using TiO_2 in slurry mode. Experiments were performed using artificial UV light coupled with ultrasound for the purpose of sonicating the slurry. The optimum conditions for better degradation of the compound were determined as catalyst dose at 1.5 gL^{-1}, pH 7 and oxidant dose at 1.5 gL^{-1} at which 80 % degradation was obtained after 120 min of irradiation. Sonication imparted synergistic effect as degradation was improved to 96 % increase after 90 min of treatment in sono photocatalysis (**Verma *et al.*, 2013**).

Fixed-bed photocatalysis

UV/TiO_2 systems are mostly used in suspension but the main problem that arises in slurry mode is the filtration of catalyst that limits its use at industrial scale. As TiO_2 is the most favorable and widely used catalyst in heterogeneous photocatalysis, it can be fixed on various supports like glass, stainless steel, pumice stone, polythene film and silica. Various studies are reported in literature using TiO_2 in the fixed-bed mode for treating the wastewater (**Pozzo *et al.*, 1997; Madani *et al.*, 2006**).

TiO_2 coating was done on stainless steel coupons and glass beads. The method followed for coating was conventional alkoxide sol-gel method and Degussa P-25 powder enriched method. Both these methods were compared. Stainless steel coupons coated with TiO_2 were used in the quartz reactor for the removal of organic pollutants present in water. SEM micrograph was prepared of stainless steel coupons immobilized with TiO_2 through powder enriched alkoxide sol-gel after three coating cycles **(Balasubramanian *et al.*, 2004)**.

Coating of the catalyst on glass rings as well as glass beads was tested for the degradation of pesticide atrazine. Two types of TiO_2 namely TiO_2 P25 and TiO_2 in colloidal form containing only anatase were used and compared for their efficiencies over degradation of pesticide. The coating of catalyst over rings and beads was done following the dip coating method. The photo catalytic degradation of atrazine with supported TiO_2 P25 over glass rings was as effective as TiO_2 in slurry mode. No significant decrease in the catalytic activity of immobilized TiO_2 over rings was observed after using the same batch for seven experiments **(Parra *et al.*, 2004)**.

TiO_2 was coated on glass plate **(Verma *et al.*, 2014a)**. The glass plate was first made rough by means of sand paper and then degreased by immersing in HNO_3 solution. The coating of TiO_2 was done following the dip coating method. The coated glass plate was calcined at 300 ^{0}C in muffle furnace for one hour. This coated glass plate was used vertically at an inclination of 20 ^{0}C and 45 ^{0}C in a reactor for the degradation of 2-chloro-4-nitrophenol. The whole setup comprising of angle variation plate and coated glass plate was kept on a movable trolley for the maximum penetration of sunlight. 72% degradation of the compound was achieved after 8 h of irradiation. The surface area using this immobilized support for photo catalytic treatment has been found to increase thus improving the degradation.

Balasubramanian *et al*., 2004 also used glass beads for the photo catalytic degradation of organic pollutants and coating of the glass beads with catalyst was done using the same method as described above in case of stainless steel. SEM micrographs of TiO_2 coated glass beads after eight coatings were prepared which demonstrates a continuous surface.

TiO_2 was immobilized on an inert support like cuddapah stone. The coating was done twice with a laboratory spray gun using the mixture of TiO_2 and acrylic emulsion. This immobilized system was used for the photo catalytic degradation of H-acid. The thin film of TiO_2 was found to be stable even after 30 days of experiments. The use of acrylic emulsion in coating improved the adherence of TiO_2 particles without bringing any change in its Photo catalytic activity. A thin film fluidized bed reactor (TFFBR) made up of cuddapah stone having dimensions: length=144 cm, breadth=52 cm and height=10 cm. the aqueous solution of H-acid was made to flow in a reactor at a flow rate of 750 mL min^{-1} using a circulation pump. Thus, TFFBR proved to be an efficient system for the degradation of recalcitrant compounds like H-acid since it prevents post-treatment filtration **(Noorjahan *et al*., 2003)**.

Subrahmanyam *et al*., 2003 carried out an investigation for the degradation of dyes and dye industry pollutants through heterogeneous photocatalysis using supported TiO_2 over pumice stones. Soaking, drying and heat treatment methods were followed for the immobilization of catalyst over pumice stone pellets. As pumice stone is a soft material, its pellets are fixed either on cement or polycarbonate. The same method of heterogeneous photocatalysis using supported TiO_2 over pumice stone was also used for the removal of pathogens from drinking water as well as for the removal of recalcitrants present in wastewater. Two reactors were designed using pumice stone pellets. One is the thin film fixed bed photo catalytic reactor. The other is the multi-tube reactor. A total volume of 8 L of solution was used in a reactor at a time having flow rate of 2 L min^{-1} under solar irradiation. Time required by such reactors for the E. Coli deactivation was 20-40 min under solar irradiation thus ensuring its technical feasibility (**Subrahmanyam *et al*., 2008)**

Rao and Chaturvedi, 2012 studied the decoloration and mineralization of wastewater from textile industries using fixed-bed photocatalysis. For the fixed-bed, they coated pebbles with TiO_2 under direct sunlight. The trough (inner length, 52 cm; inner width, 45 cm; height, 0.8 cm) was made up of transparent Perspex sheet. The pebbles were placed uniformly forming equilateral triangles which leads to the optimal distribution of liquid over the pebbles thus avoiding preferential channeling

Studies have been conducted for coating quartz sand with TiO_2 P25 **(Heinzle *et al*., 1996)**. Coating was carried out in 2-propanol thus making a suspension of TiO_2 and quartz sand which was air-dried after filtering and washing with 2-propanol. The coated quartz sand was then heated at 400 ^{0}C for 1 h. This coated quartz sand was loaded in fluidized bed photoreactor and the degradation of 4-chlorophenol and p-toluenesulfonic acid was investigated.

Studies are reported regarding coating of TiO_2 on fiber **(Stephan *et al*., 2011)**. Coated fiber was deposited on the steps in the falling film closed loop step reactor. These studies were conducted for the degradation of pesticide chlortoluron. Satisfactory results were obtained regarding the degradation of compound but still some improvements are required in case of commercial applications.

A hydrosol dip coating method was used for coating quartz optical fibers and quartz rods **(Hoffmann *et al*., 1995)**. Three coatings were found to be sufficient for efficient coating. These coated fibers and rods were fired at high temperature ranging from 200 ^{0}C and 500 ^{0}C in a muffle furnace. An optical fiber reactor bundled with the coated fibers was employed for the photo catalytic degradation of 4-chlorophenol.

Thin film coating of the catalyst is a widely used method for the photo catalytic degradation of organic pollutants. **Zayani *et al*., 2009** made use of a thin film fixed-bed reactor for the photo catalytic degradation of commercial textile azo dyes. After proper stirring, TiO_2 suspension was applied to the outer surface of the concrete plate using a painting roller which was then left under solar radiations for one day.

Cemented slabs were coated with TiO_2 and were used in photo catalytic experiments to study the degradation of 2-chloro-4-nitrophenol. Coating was done following the dip coating method. 75 % degradation was achieved using this support material. Catalyst was found to be stable after reuse. The same slabs were used for at least ten experiments and were found to be durable enough **(Verma *et al*., 2014a)**.

TiO_2 was immobilized on cement beads of different diameters and their efficacy was checked for the degradation of herbicide isoproturon. Coating of TiO_2 on beads was carried out using standard dip coating method. Two cycles of coating were repeated using the same method and after every cycle, beads were calcined at 400 ^{0}C for two hours in muffle furnace. The same coated beads were used in solar baffled reactor to study the degradation of the compound and significant degradation was achieved using the immobilized beads **(Verma *et al.,* 2014c)**.

Doping of TiO_2

Different methods have been proposed for the preparation of doped TiO_2 **(Loganathan *et al.,*2011).**

Primo *et al.,* 2010 reviewed about the photo catalytic properties n preparation techniques for doping of gold nano particles on TiO_2. The photo catalytic activity of Au/TiO2 was the main focus of the research for hydrogen generation, dye discoloration and carboxylic acid degradation. It was concluded that Au/TiO2 photo catalysts has good scope in the near future for environmental remediation.

Frenso *et al.,* 2005 made Sn doped TiO2 samples and studied the photo catalytic degradation of chlorsulfuron (ChS), a herbicide.
Three synthesized photo catalysts were used, two of them containing 11 and 20 mass% of Sn, respectively, and one composed of pure anatase TiO_2. Adsorption observations showed that, an inverse dependence of the photo catalytic activity on the water adsorption capacity of the samples was observed.

Platinum doped TiO_2 was spread on the surface of glass film by spray gun on the pipe of drum. Target compound to be degraded was aqueous phenol and it was observed that there was no change in the structure of film after operating it for more than 2000 hours. Also high degradation rate was observed under artificial light as compared to the solar light **(Zhang *et al.,* 2001).**

Jeffery et ***al.,*** **2004** prepared vanadium-doped TiO_2 catalysts using sol–gel method. The photo catalytic activity was monitored by the degradation of and Methylene Blue (MB) and also Crystal Violet (CV) under irradiation of visible light. The degradation rate of both the dyes was higher than those of pure TiO_2.

TiO_2 nano particles doped with silver were prepared using sol–gel method and were used as photo catalysts in the photo catalytic degradation of a pesticide Acetamiprid. The presence of silver in crystalline TiO_2 helped in increasing the photo catalytic activity of the catalyst, with the photo catalytic degradation velocity constant (k) rapidly increased when the silver content increased from 0.02 to 0.06 **(Yongsong *et al.,*2008).**

Sol–gel method was used for the preparation of Nitrogen doped TiO_2. The photo catalytic activity of doped TiO_2 was measured under UV and visible light using lindane,which is an insecticide as a target pollutant. Triethylamine which was used as nitriogen source,doped with TiO_2 showed excellent results in the degradation of lindane under visible light**(Senthilnathan *et al.,*2010).**

Reddy ***et al.,*** **2010** prepared C, N, and S doped TiO_2 photo catalyst and studied the role in photo catalytic degradation of pesticides. It was concluded that 5 wt% thiourea doped TiO_2 is a effective catalyst for the degradation of isoproturon. The substrate concentration of $1.14 \times 10{-}4$ M, catalyst amounts 1 g L^{-1} and neutral pH were found to be favorable for better degradation rates of isoproturon.

Chapter 3
Research gaps

Based on literature review the following research gaps have been observed:-

1. There is very limited study on the degradation of compounds like 4-chloro phenoxy acetic acid through heterogeneous photocatalysis.
2. There is still scope of research in selecting the innovative, cheap and effective support material for catalyst immobilization.
3. Durability of the supported material to be used for at-least 50 recycles and the choice of supported material are the major concerns to be looked carefully for field scale applications.
4. There are only few studies that have been carried out on the degradation of herbicides using doped TiO_2.
5. Very few studies have been conducted so far for the degradation of organic pollutants by immobilizing doped catalyst on some inert support materials.

Chapter 4

Objectives

The study is undertaken with the following objectives:-

- Degradation and mineralization studies of 4-chlorophenoxyacetic acid through slurry photocatalysis using TiO_2 and doped TiO_2 and optimization of operating parameters like catalyst dose, oxidant addition, pH, UV intensity, depth of reactor.
- Catalyst immobilization for doped/un-doped using clay beads as inert support for the degradation of 4-chlorophenoxyacetic along with parametric studies like number of coatings, bead size, calcination temperature etc.
- Durability studies of support material in terms of number of recycles with respect to the immobilization of both forms of catalyst.

Chapter 5

Materials and methods

This section discusses about the various analytical methods used for the treatment of compound. Standard methods have been employed throughout the study.

5.1 Pesticide

4-chloro phenoxyacetic acid ($C_8H_7ClO_3$) (fig: 5.1) commonly known as 4-cp was purchased locally from the market ,Patiala (India). 4-CPA is a synthetic pesticide which belongs to chemicals in a group of plant hormones referred as auxins. It is being detected in wastewater at low concentrations and being highly stable and low biodegradability, it is difficult to remove through conventional techniques.

Maximum absorbance of the compound was obtained at 275 nm after scanning it through UV- Vis spectrophotometer over a range of 190 to 450 nm.

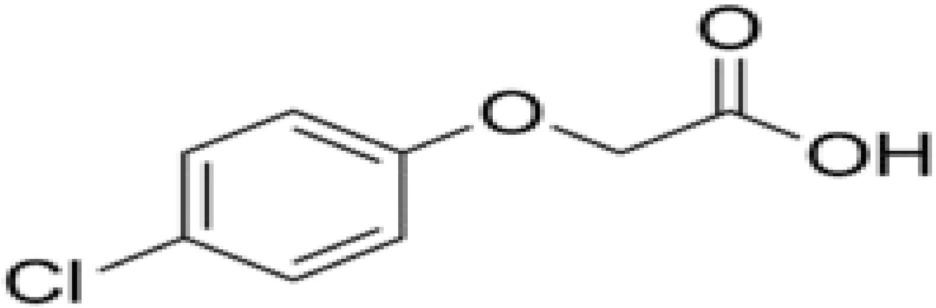


Figure 5.1: Chemical structure of 4-CPA.

5.2 Reagents and chemicals

TiO_2 P-25 was used as a photo catalyst and was attained from Evonik Industries, India. Hydrogen Peroxide, H_2O_2 used as an oxidant was from Ranbaxy, India. The concentrated solutions of NaOH and HCl are used for setting the pH were obtained from Merckall solutions were prepared using double distilled water. Standard methods were used for calculating chloride and COD.

5.3 Instruments used

5.3.1 pH meter

The pH meter (purchased from Eutech instrumentation) was used to adjust the pH of the solution using 0.1N HCl and 0.1N NaOH. Instrument was calibrated weekly with freshly prepared buffer solutions (pH 4 and 9).

5.3.2 UV-Vis Spectrophotometer

UV-Vis spectrophotometer (LABINDIA, model no. T60 U) was used for photo degradation analysis of 4-cpa at 275 nm.

5.3.3 Radiometer

Eppley (model no. 33013) radiometer was used to measure solar UV Intensity hourly during experimental days.

5.3.4 Branson bath sonicator

Ultrasonic bath Tank (model no. EN 60 US) with frequency of 33 KHz was used for homogenization of catalyst suspension in the process of catalyst coating on clay beads.

5.3.5 Muffle Furnace

Rate controlled muffle furnace (temperature range 200 to 1200 ^{0}C) was used for the fixation of catalyst coating on clay beads. It was operated at a temperature of 250 ^{0}C for this purpose.

5.3.6 COD Digester

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

5.4 HPLC analysis

HPLC was also used for analyzing the sample for the confirmation of 4-cpa degradation. HPLC was performed on binary HPLC system with C-18 column (100 mm x 2.1mm), particle size 2.6µm using MeOH and formic acid was used as mobile phase with UV detector at 275 nm for 4-CPA. 400µL min^{-1} was maintained as the flow rate with 0.1% formic acid. the injection volume was 5µL and each analysis lasted for 18 min.

5.5 SEM-EDAX analysis

The morphology of freshly coated clay beads and recycled beads was studied using SEM (JSM-6510LV, JEOL, Japan) and EDS (INCAX-act, Oxford instruments, United Kingdom).

5.6 GC-MS

Gas chromatograph (45X-GC, Bruker) is integrated with the mass detector (MS-SCION-45P, Bruker) and with MS wax column with diameter and length of 0.25 m and 30 m. Helium is the carrier gas with a flow rate of 1.0 mL min^{-1}. 80–410 was used as the range for scan. 280˚C was the injection temperature. The temperature of GC oven was set from 40 to 260 ˚C with 10 degree increase in temperature 1: 10 GC split ratio was employed and 1.0 mL sample was injected automatically.

5.7 Experimental setup and procedure

5.7.1 Lab scale reactor setup

For performing the photo catalytic experiments, rectangular wooden UV chamber was used **(Verma et al., 2014)**. The batch reactor is made of borosil glass and 5.2 cm in height and 17.4 cm in diameter with capacity of 1200mL. The reaction bowl is placed at loratory jack in a rectangular wooden UV chamber having dimensions 1.37 m × 0.9 m × 1.0 m. The chamber contained 36 W UV tubes having wavelength of 365 nm and were installed on the underneath of the chamber. The required UV intensity could be achieved by varying the distance of reactor from UV tubes (**Toor et al., 2006)**. The UV intensity was changes from 10 to 25 Wm^{-2}. For controlling the temperature of the chamber, it is equipped with exhaust fan .The reaction was carried out in natural solar light as well. Slurry was made by dissolving sufficient amount of 4-CPA in double distilled water and it was magnetically stirred at 30-40^{o}C for about 2 hours. The solution was prepared weekly and stored at room temperature.

For the photo catalytic experiments, the 4-CPA solution was kept in dark (1 h) to get the complete adsorption equilibrium. A 200mL of the antibiotic aqueous solution was taken in a batch reactor with sufficient amount of TiO_2 and was kept under UV radiation with constant stirring. spargers provided the aeration. Sample of 3-4mL was collected at regular time intervals from the vessel using a syringe and was filtered from Millipore filter (0.45 µm). Figure 5.2 (a) and 5.2 (b) shows the pictures of the slurry batch reactor setup in artificial UV light and natural sunlight respectively.

The parameters were varied like concentration of catalyst, amount of oxidant, pH, UV intensity, reactors depth based on which reaction kinetics was decided. All experiments were carried out in triplicate for confirming the results. The standard deviation for all the reactions was between the ranges of 2-6%.

Figure 5.2(a): Lab-scale setup of slurry reactor in UV light.

Figure 5.2(b): Lab-scale slurry reactor in sunlight.

5.7.2 TiO_2 coated clay beads

5.7.2.1 TiO_2 immobilization

Around 400 clay beads of different size were prepared manually by mixing clay. From these beads, almost 300 beads of uniform size were selected and used for TiO_2 coating. TiO_2 was coated on clay beads using method described in previous studies **(Verma et al., 2014)**. Even the previously coated TiO_2 beads used in earlier study were also used for checking their efficiency in degrading the 4-CPA.The catalyst was coated on the surface of beads as film with average thickness of 40µm and this was confirmed from SEM-EDS. Figure 5.3(a) shows the image of freshly coated TiO_2 clay beads and Figure 5.3(b) shows the image of used TiO_2 coated clay beads.

Figure 5.3(a): TiO_2 freshly coated clay beads.

Figure 5.3(b): Used TiO_2 coated clay beads.

5.7.2.2 Doping of TiO_2 nano particles

Iron and Copper anatase/brookite TiO_2 powders were prepared using acid catalyzed sol-gel method. Acidic solution as a precursor was prepared by mixing certain amount of nitric acid and distilled water (90ml, pH 2.5), this is solution A. 14.8 ml of Titanium tetraisopropoxide ($Ti(OC_3H_7)_4$), Sigma-Aldrich, 97%) was diluted in 80 ml of isopropanol. In this solution, 1% and 2% of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ (Sigma-Aldrich, 99.99%) were added according to the required Fe/Ti and Cu/Ti atom ratio (solution B). Solution A is then added drop wise to solution B with constant and vigorous stirring for 24h time span. This mixture was kept for 12 h, washed and filtered several times with de ionised water. Then the final product was dried at 50°C. The resulting powders were calcined for 2h.

Although doped and co doped catalysts were provided directly.

5.7.2.3 Experimental procedure

Fixed-bed photo catalytic studies were done using same batch reactor containing required amount of catalyst coated cement beads and 200mL of pesticide solution. This reactor was irradiated under UV light. Aeration was provided by means of two spargers at a time. The samples were collected by means of a syringe at regular intervals. The lab-scale setup is shown in figure 5.4.

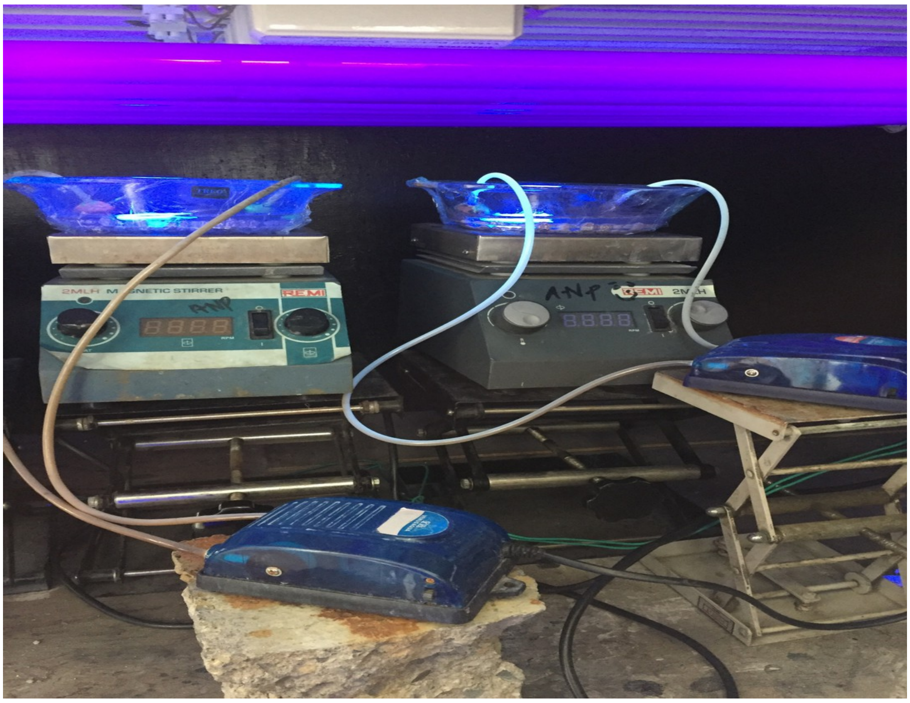


Figure 5.4: Lab-scale setup of fixed-bed reactor.

CHAPTER 6

RESULTS AND DISCUSSION

The photo catalytic degradation of 4-CPA using slurry and fixed-bed photocatalysis employing TiO_2 has been discussed in this chapter. Process parameters have been optimized by varying certain parameters like concentration of oxidant, catalyst dose, intensity of UV pH, and A/V ratio. Studies were also carried out using TiO_2 doped with copper and iron.

6.1 Standard calibration curve of 4-CPA

Standard calibration curve was plotted using known concentration of 4-CPA. A graph of absorbance versus concentration of 4-CPA solution was plotted by varying the known concentration of the solution as shown in figure 6.1. The concentration of 4-CPA solution was varied from10 mgL^{-1} to 100 mgL^{-1}. The regression coefficient and slope of the curve were found to be 0.999 and 0.0072 respectively.

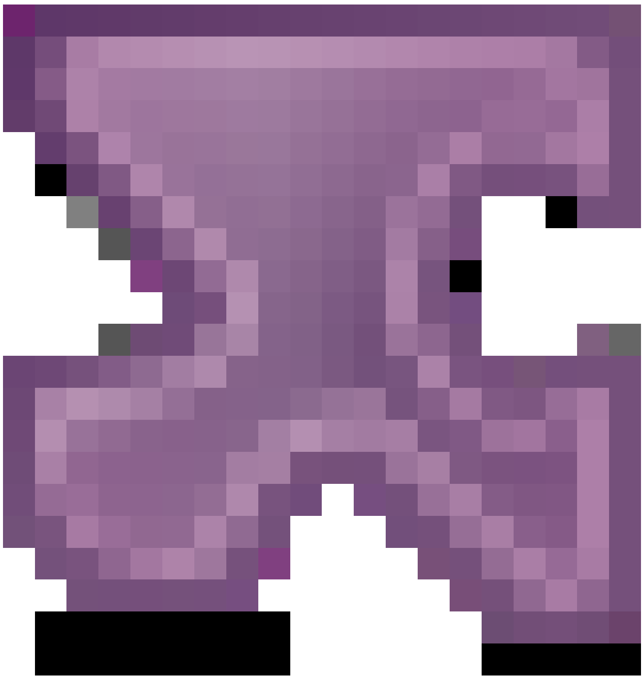


Figure 6.1: Standard calibration curve of 4-CPA.

6.2 Degradation studies of model compound using slurry photocatalysis

6.2.1 Preliminary studies

Preliminary reactions were conducted to study the effect of individual operational parameters on the degradation rate of 4-CPA. A negligible amount of photo degradation (7.8%) was observed when only 4-CPA aqueous solution was irradiated under UV light in a batch reactor. The slurry reaction was kept in dark with sufficient amount of TiO_2 and the reduction in concentration of the model compound is mainly due to the adsorption (15%) on the catalyst surface. Moreover, when H_2O_2 alone was used, 10% degradation was attained which might be due to the production of very less OH radicals. The photo catalytic treatment (UV + TiO_2 + H_2O_2) of 4-CPA showed significant degradation i.e. 93% after 90 min (Figure 6.2) due to the substantial increase in the generation of hydroxyl radicals. Thus, it leads to an assumption that adsorption and desorption of model compound and formation of reaction intermediates are slower than the generation of electron/hole pairs.

Figure 6.2: Photo catalytic degradation of 4-CPA in the presence and absence of TiO_2, H_2O_2 and UV. Experimental conditions: C_0=100 mgL^{-1}, V = 200 mL, UV intensity = 25 Wm^{-2}.

6.2.2 Photo degradation Kinetics

Various kinetic models have been defined for the photo catalytic degradation of different organics. Langmuir-Hinshelwood (L-H) kinetics model is the most acceptable model for almost all photo catalytic reactions. According to L-H model, the rate of degradation of organic pollutants is stated by equation 1.

$$-dC/dt = k_r KC/(1 + K C) \qquad (1)$$

Where, k_r is the reaction rate constant, K is the equilibrium adsorption constant; C is the substrate concentration at any time t. The factor KC being very small at low substrate concentrations can be neglected. Almost all the photo catalytic experiments followed pseudo-first order kinetics according to L-H model for studying the degradation of various organic compounds over TiO_2 (equation 2), i.e., $-dC/dt = kC$

$$\text{Or } \ln C_0/C = kt \qquad (2)$$

6.2.3 Effect of TiO_2 concentration

An appropriate concentration of TiO_2 is required for the photo catalytic experiments. However, high concentration of catalyst is not recommended as it becomes difficult to separate the catalyst from slurry at higher concentration and moreover, it makes the process more expensive. In our study, concentration of TiO_2 was varied in the range 0.25-0.875 gL^{-1}. Photocatalysis of 100 mgL^{-1} of 4-CPA was done for three hours at its natural pH i.e. 3.5. Figure 6.3 demonstrates that the degradation rate constant (k) initially increased from 0.004 to 0.0102 min^{-1} by increasing the TiO_2 concentration up to 0.875 $gL^{-1}$and then decreased with further increase in photo catalyst concentration. The probable reasons might be the reduction in the light penetration, enhanced scattering of light **(Kansal et al., 2007)**, formation of aggregates and settling of catalyst under high concentration **(Kilic et al., 2007)**. The decrease in photo catalytic reaction rate owed to OH radicals reduction due to above cited factors. The best suitable amount of catalyst selected was 0.625 gL^{-1} of TiO_2 at which approximately 85.53% degradation was achieved after irradiation of 3 hrs. Although in the given graph the degradation is shown for 2 hours as the degradation rate became almost constant after 2 hours.

Object 7

Figure 6.3 (a): Plot of ln C_0/C vs time at different concentrations of TiO_2

Object 9

Figure 6.3(b): Plot of first order rate constant, k Vs variation in TiO_2 concentration during photo catalytic degradation of 4-CPA (C_0= 100 mgL^{-1}, V= 200 mL).

6.2.4. Effect of pH on degradation of model compound

In order to observe the effect of initial pH on photo catalytic removal of 4-CPA, pH was altered in the range of 2.5-9.5 with optimized conditions i.e. TiO_2 0.625 gL^{-1} with $C_o = 100$ mgL^{-1}. The initial pH of the reaction solution shows the adsorption of the compound and surface charge characteristics of catalyst. At acidic pH, the surface charge of TiO_2 is positive and becomes negative at basic pH **(Toor et al., 2007)**. Thus, pH plays an important part in the adsorption/desorption characteristics of the catalyst **(Hoffman et al., 1995)**. The rate of degradation in the present study was maximum at its natural(acidic) pH i.e. 3.5 and thereafter a considerable decrease in the degradation rate was observed at alkaline pH as 'k' was considerably higher (0.02 min^{-1}) in acidic pH as compared to k value (0.001 min^{-1}) in basic pH as depicted in the Figure 6.6. All studies were conducted at solution's natural pH i.e. 3.5 at which approximately 93% degradation was attained under optimized conditions. Although in the given graph the degradation is shown for 2 hours as the degradation rate became almost constant after 2 hours.

Object 11

Figure 6.4 (a): Plot of ln(C_0/C) versus time at different pH for the photo catalytic degradation of 4-CPA

Object 13

Figure 6.4(b): Plot of first order rate constant, k Vs variation in pH during photo catalytic degradation of 4-CPA (C_0= 100 $mgL^{-1,}$ V= 200mL).

6.2.5 Effect of H_2O_2 addition

The role of oxidant (H_2O_2) in increasing the rate of photo degradation is now evident and well established in literature **(Malato et al., 2000; Poulios et al., 2003)**. Actually, presence H_2O_2 generates $^{\cdot}OH$ radical when the photon excited electron from the conduction band is accepted. It leads to the generation of $^{\cdot}OH$ radicals according to reaction (1) **(Kositzi et al., 2004)**.

$$H_2O_2 + {}^{\cdot}O_2^- \rightarrow {}^{\cdot}OH + OH^- + O_2 \qquad (1)$$

In order to calculate the optimum concentration of H_2O_2, the experiments were carried out by varying the initial concentration of H_2O_2 from 0.05-0.2mL/200mL with optimum TiO_2 concentration of 0.625gL^{-1} and at natural pH of the solution i.e. 3.5. Photo catalytic degradation rate constant (k) varied from 0.013 min^{-1} to 0.019 min^{-1} and with increasing addition of H_2O_2 from 0.05-0.2mL (Figure. 6.4). The degradation increased to 93% with the addition of 0.125 ml/200mL of H_2O_2. The degradation rate constant (k) started decreasing after 0.125mL of H_2O_2. The possible reason may be the scavenging of $^{\cdot}OH$ and hole which forms HO_2 as shown in reactions (2) and (3) **(Zhao et al., 2004; Behnajady et al., 2006)** at high concentrations of H_2O_2.

$$^{\cdot}OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (2)$$

$$H_2O_2 + h^+ \rightarrow H^+ + HO_2^{\cdot} \qquad (3)$$

Therefore, the best suitable amount of oxidant selected was 0.125mL of H_2O_2 which resulted in 93% of degradation after 3 hrs of irradiation at 0.625gL^{-1} of TiO_2 at its natural pH i.e.3.5. These optimized conditions were employed for further experiments. Although in the given graph the degradation is shown for 2 hours as the degradation rate became almost constant after 2 hours.

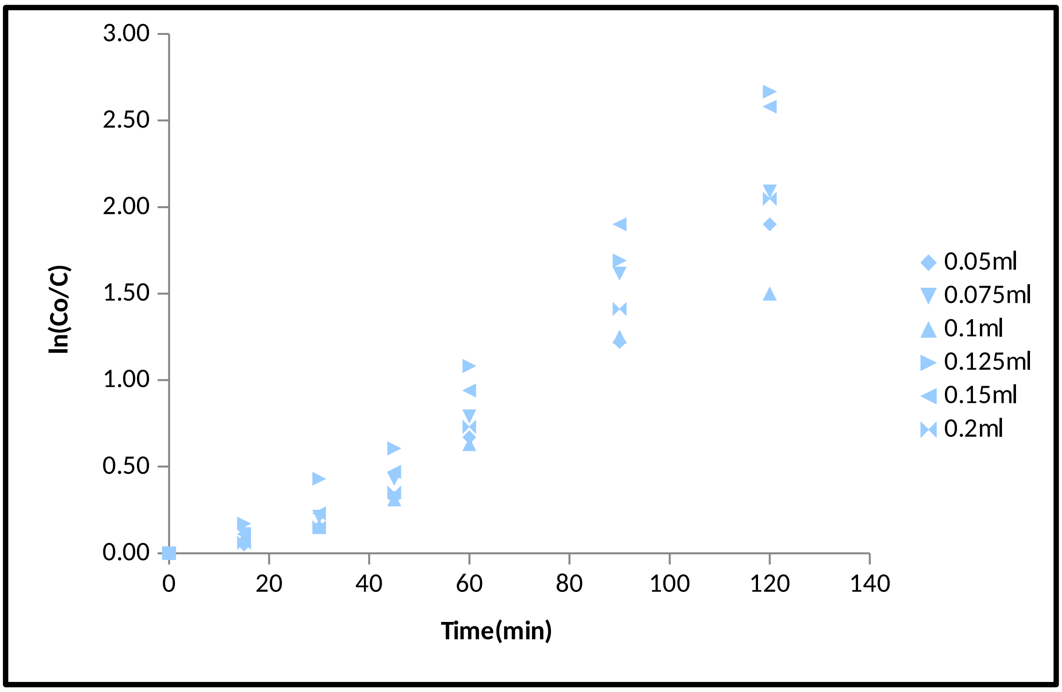


Figure 6.5 (a): Plot of ln C_0/C versus time at different concentrations of H_2O_2 for photo catalytic degradation of 4-CPA.

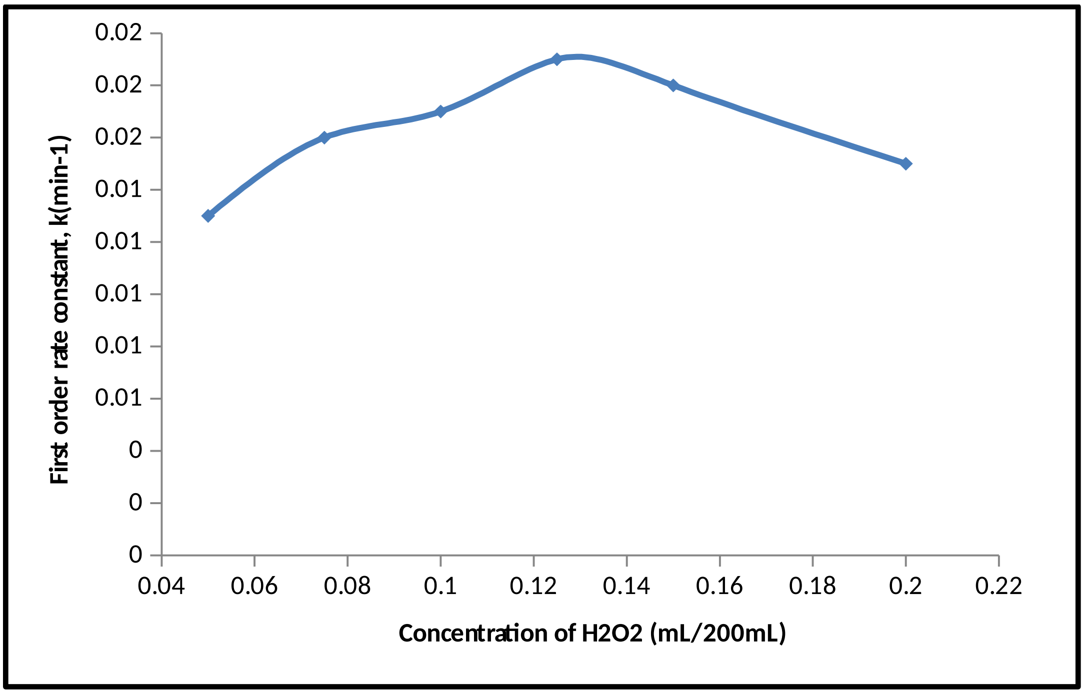


Figure 6.5(b): plot of first order rate constant, k Vs varying H_2O_2 dose during photo catalytic degradation of 4-CPA (C_0= 100 mgL^{-1}, V= 200mL, TiO_2=0.625gL^{-1})

6.2.6 Effect of UV intensity

Utilization of solar radiations for degrading contaminants is the most important application of AOP. Throughout the year the intensity of solar radiations is not constant.**(Dubey et al., 2009)**. Optimized concentration of catalyst and H_2O_2 was added into the 100 mgL^{-1} aqueous solution of 4-CPA and irradiated under Uv light while keeping A/V constant at 1.13 cm^{2}mL^{-1}. An increase in the rate constant from 0.001 to 0.102 min^{-1} was observed with increasing intensity of UV from 10 to 25 Wm^{-2} (Figure 6.5). The possible reason may be the production of more OH radicals.

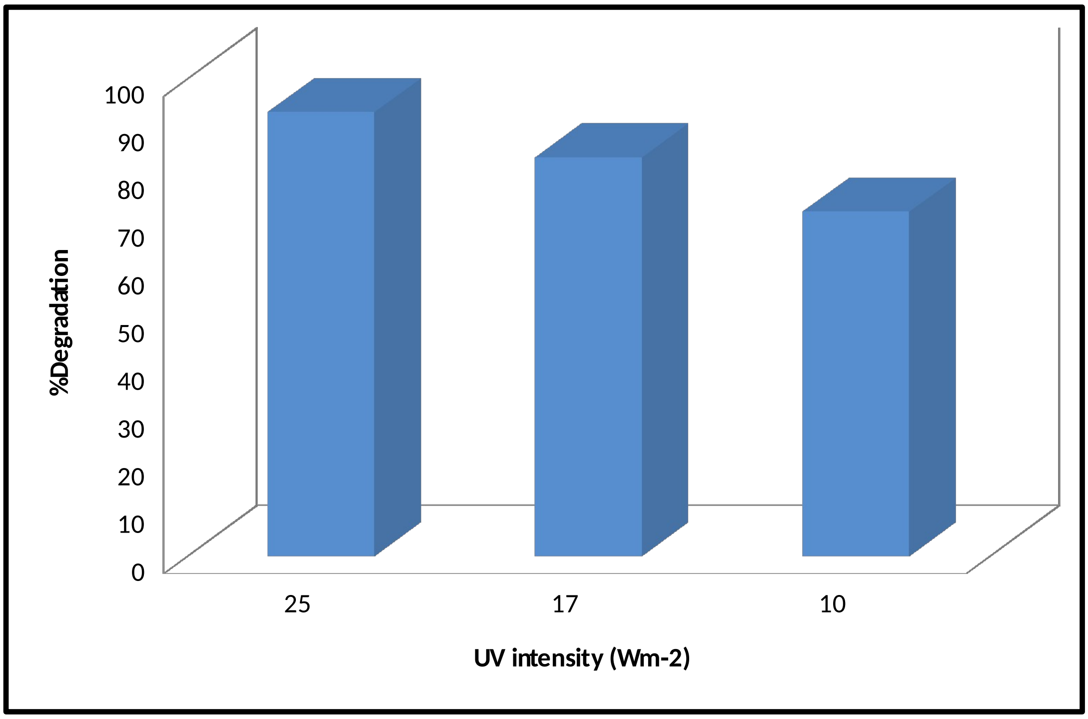


Figure 6.6: photo catalytic degradation of 4-CPA by varying UV intensity (C_0= 100mgL^{-1}, V= 200mL).

6.2.7. Effect of Area/Volume Ratio of Batch Reactor

For field-scale application one of the major limitations of AOP is the obstruction of depth of reactor for the penetration of solar radiations. Less depth and more exposed area is generally recommended for the effective penetration of solar light **(Toor et al., 2006)**. This can be achieved by varying area of the reactor and keeping the volume constant or volume of solution to be treated can be varied while keeping the area constant. In the present study, the Area/Volume (A/V) of batch reactor was varied from 0.648-4.53 cm^2 mL^{-1} while varying the volume of solution and keeping the aperture constant. A noticeable increase in degradation was achieved by increasing the A/V ratio as 'k' changed from 0.0072 to 0.0263 min^{-1} as shown in figure 6.7. Depth of the solution decreases by increasing the A/V which leads to path length increase of photons entering the reaction solution which results in higher yield of OH radical thereby improving the photo catalytic performance **(Verma et al., 2014)**. At lower penetration of light, electron-hole recombination is more which decreases the yield of hydroxyl radicals thereby reducing the degradation rate. However, A/V ratio of 1.1343 cm^2 mL^{-1} was used for further experiments.

Figure 6.7 (a): Plot of ln C_0/C vs time at different A/V ratio for the photo catalytic degradation of 4-CPA

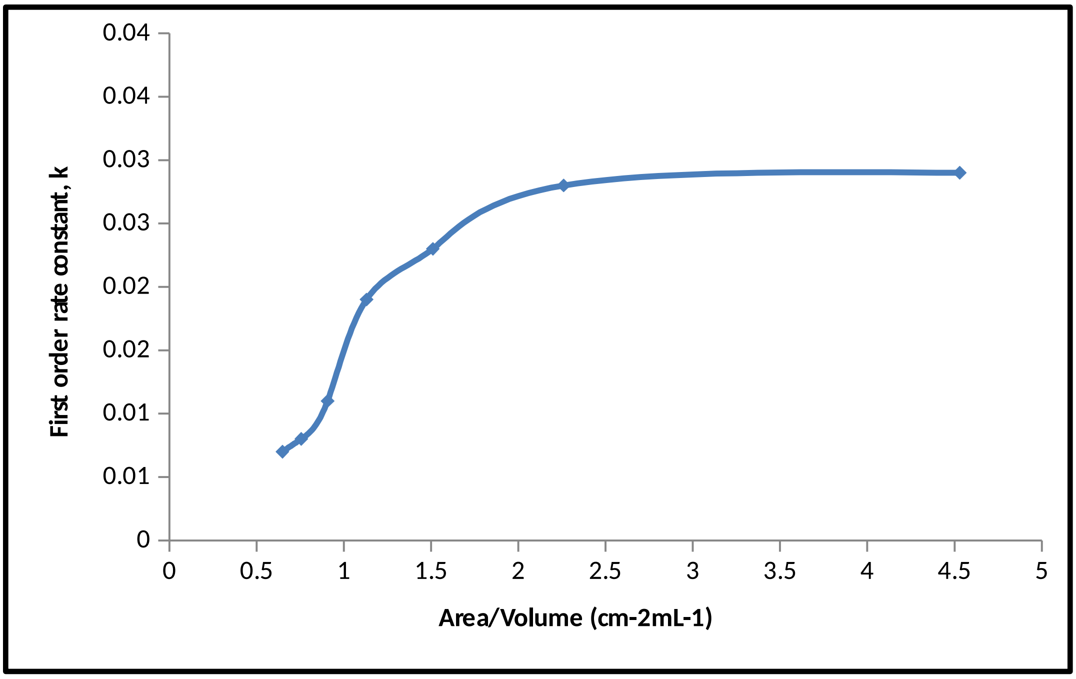


Figure 6.7(b): Plot of first order rate constant, k Vs effect of A/V ratio during photo catalytic degradation of 4-CPA (TiO_2 = 0.625gL^{-1}, C_0=100 mgL^{-1})

6.2.8 Solar versus artificial UV irradiation

The cost of energy source is always a barrier for field-scale applications of advanced oxidation processes. The capital cost of the process can be minimized by the use of natural solar radiations instead of artificial UV light. In the current study, the photo catalytic experiments were carried out in sunlight also and the effect of both artificial UV and natural solar irradiation on the percentage degradation of 4-CPA was compared. The reaction conditions were optimized under simulated UV irradiations and these conditions were used for solar experiments. The percentage degradation was increased to 99% when photocatalysis was carried out in natural sunlight while 93% degradation occurred when irradiated in artificial UV light as demonstrated in figure 6.8. Hence, the technology used in the study is economically feasible and can also give a viable solution to the industries for treating recalcitrant compounds.

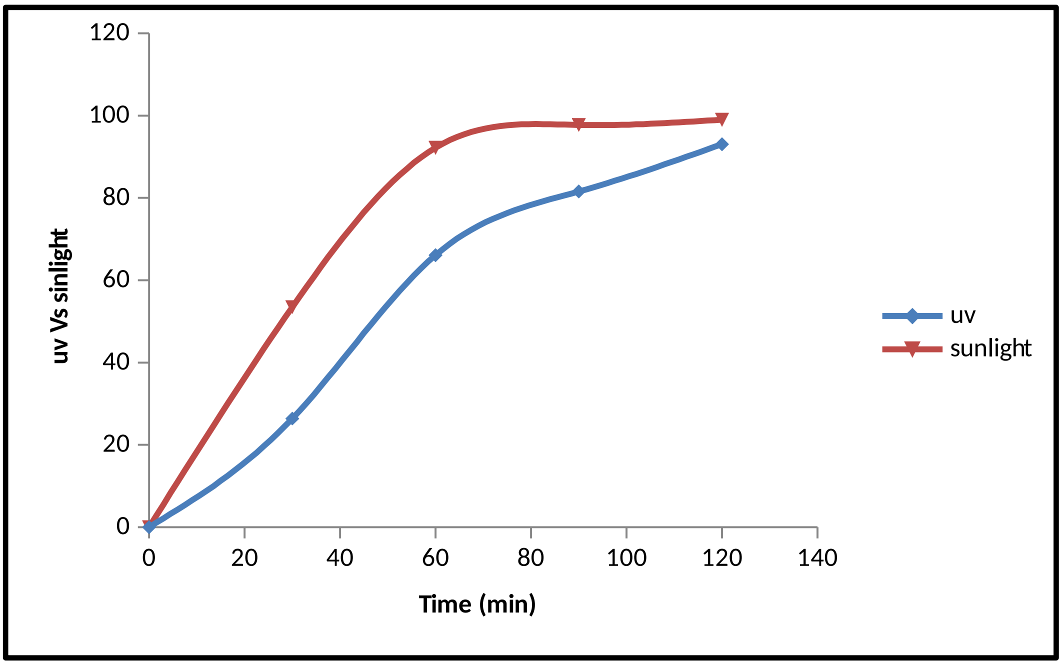


Figure 6.8: Effect of artificial UV and natural solar irradiation on degradation of 4-CPA

6.3. Mineralization studies

Formation of inorganic anions and cations with the generation of CO_2 generally indicates the complete mineralization of compounds during photo catalytic treatment (**Evgenidou et al., 2005)**. In this context, reduction of COD and generation of chloride ions were monitored for studying mineralization of 4-CPA under optimized conditions, 85.7% COD reduction was achieved after three hours. Also generation of chloride ions was first maximum and then became constant after 1 hour. Moreover, disappearance of peak for the parent compound at

279 nm was indicated in HPLC chromatograms. In chromatogram, absence of other peaks confirmed that either they were completely mineralized or no intermediates were formed.

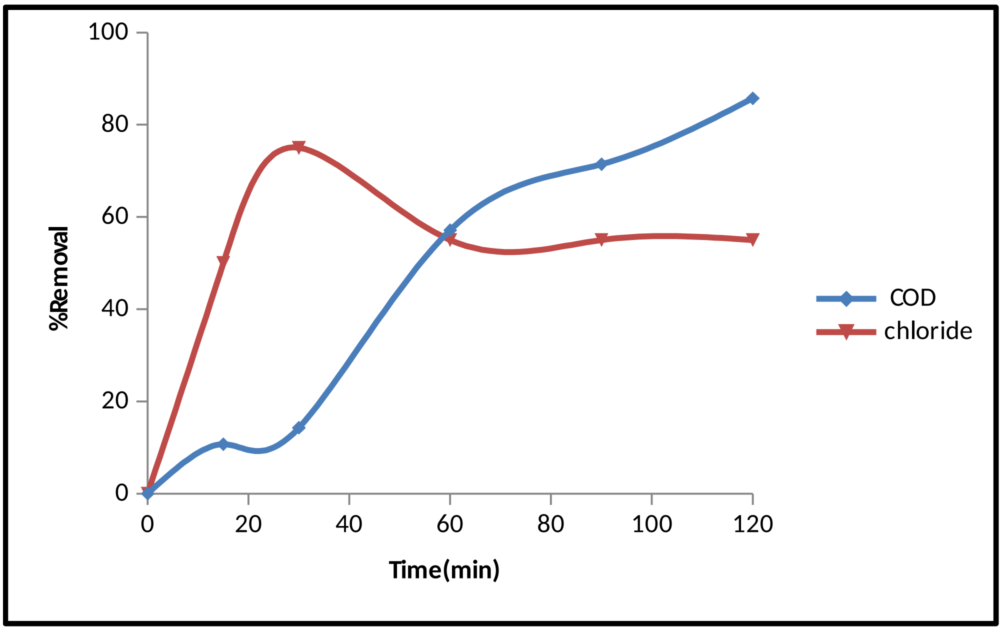


Figure 6.9: COD and Chloride reduction during the photo catalytic degradation of 4-CPA

6.4 Degradation studies of model compound using fixed-bed photocatalysis

The major problem with slurry photocatalysis regarding field-scale applications is the separation of catalyst from the treated solution. Benefits of high degradation in slurry are always compensated due to high filtration cost. In this context, efforts have been done to study the degradation of 4-CPA using fixed-bed catalysis with clay beads coated with TiO_2 **(Verma et al., 2014)**. The amount of H_2O_2 was varied from 0.1 ml-0.9 ml also buffer of pH 3.5 was added to keep the pH of the solution constant. Maximum degradation of 97.16% was achieved by adding 0.7ml of H_2O_2. Although, when simple reaction was carried out on TiO_2 coated clay beads, degradation achieved was only 77%.

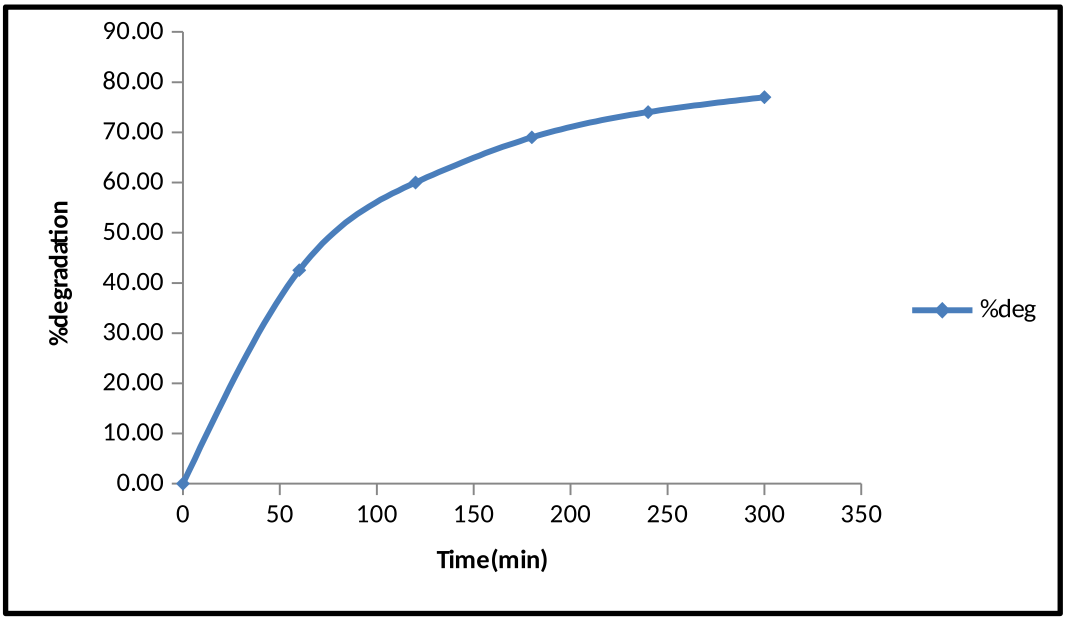


Figure 6.10(a): Plot of %degradation Vs time during fixed bed photo catalytic degradation of 4-CPA

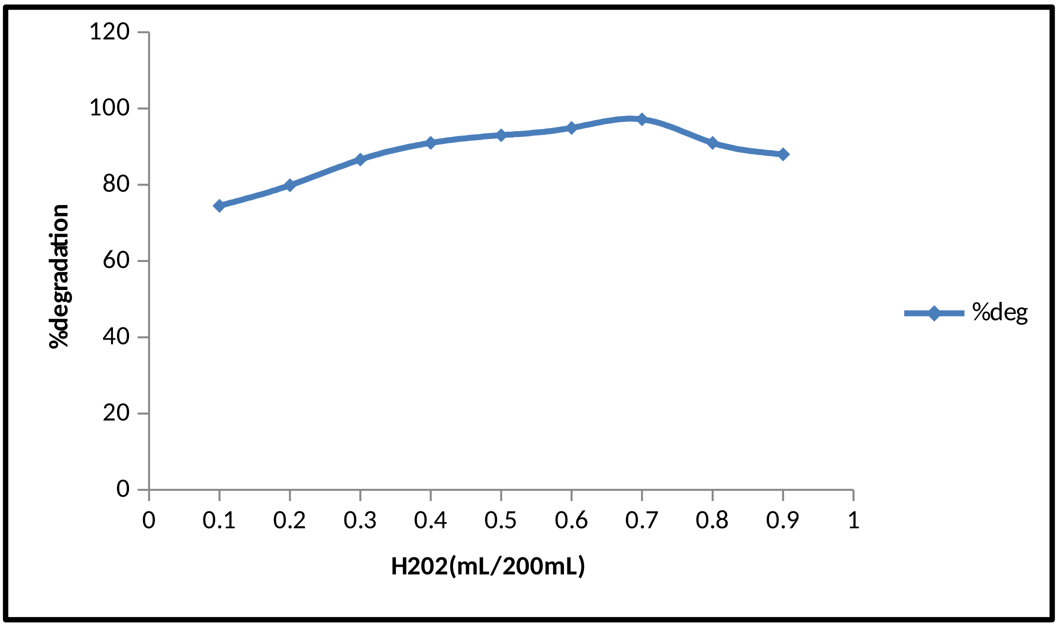


Figure 6.10(b): Plot of %degradation Vs varying H_2O_2 during fixed bed photo catalytic degradation of 4-CPA

6.4.1 Durability studies

In fixed-bed photocatalysis, durability of support material is very significant. Generally, after certain runs the activity of supported catalyst reduces **(Parra et al., 2004)**. The coated catalyst can be re-activated using at temperature 480°C, although which is practically difficult. In the present work, efforts have been done to check the durability of fixed catalyst on clay beads for the degradation of 4-CPA. The clay beads were recycled for thirty to forty times without any much decrease in the degradation of target compound as shown in Figure 6.11 (a)., the clay beads were heated in oven at 100°C for the period of 60 mins for re-activation. Decrease in degradation efficiency of clay beads is due to blocking of certain catalytic sites or loss of catalyst during subsequent reactions. Stability of the catalyst on the surface of clay beads was confirmed by SEM-EDS results which demonstrated that even after thirty cycles the catalyst was in the form of film and intact (Figure 6.11 (b)).

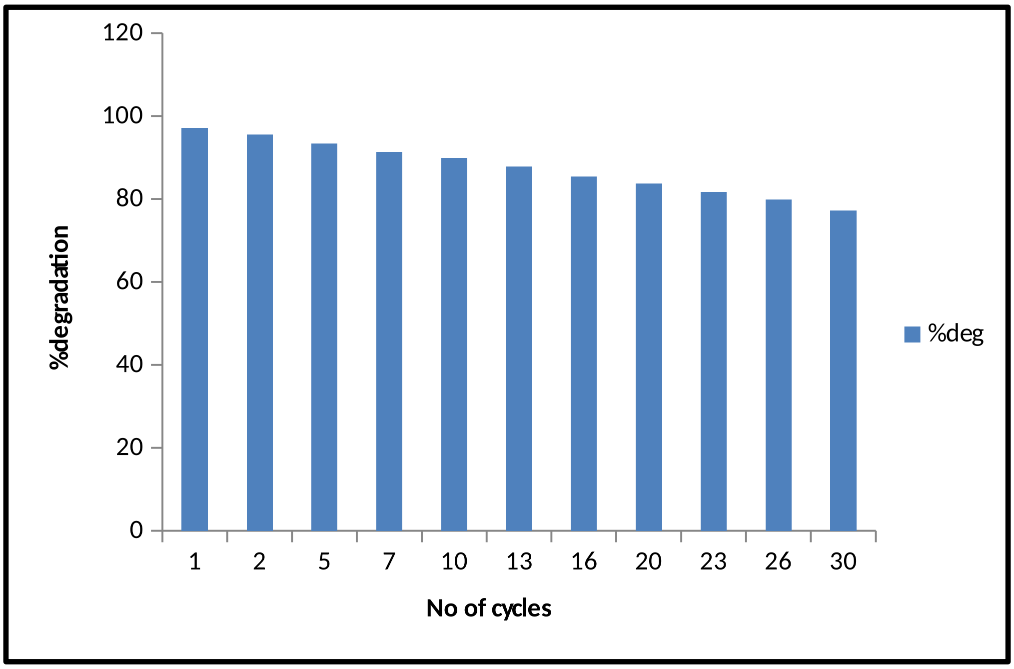


Figure 6.11(a): Durability studies of catalyst coated clay beads for the fixed-bed photo catalytic degradation of 4-CPA.

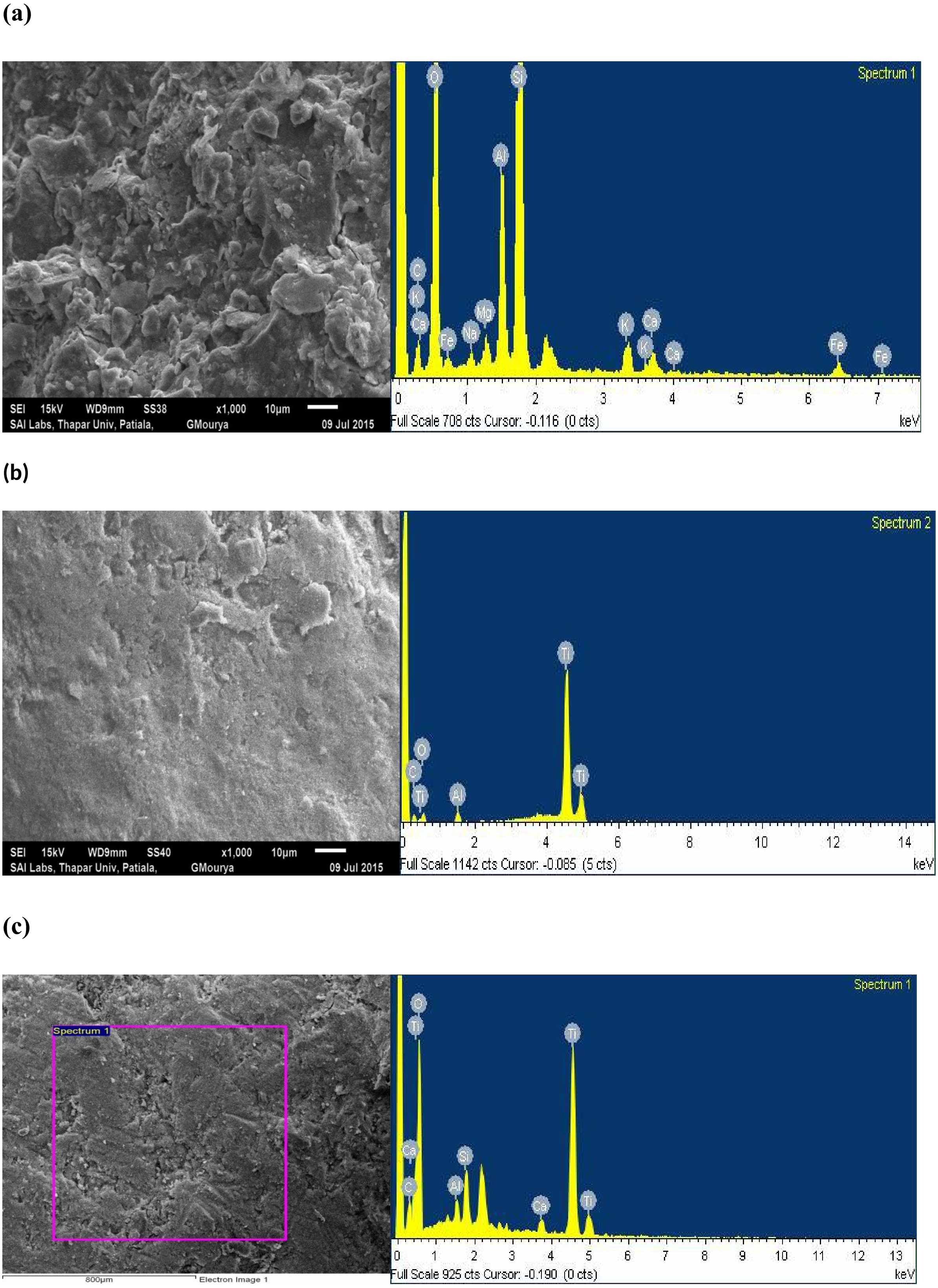


Figure 6.11(b): SEM images (a) blank clay bead without TiO_2 coating (b) freshly coated TiO_2 clay bead (c) used clay bead after 30 cycles along with their EDS data.

6.4.2 Effect of number of beads

Effective surface area available for any photo catalytic reaction is very important as far as degradation of target compound is concerned. In present study, the number of catalyst coated beads was varied in terms of percentage of the area covered by them and correspondingly degradation of the 4-CPA was analyzed. It was observed that best degradation (92.48%) was achieved when one hundred and sixty five beads were uniformly placed in the bowl covering the entire bottom surface of the bowl (with no overlapping) as all catalyst binding sites were available to bind the pollutant leading to efficient degradation. While, approximately 83% degradation was attained when eighty five beads were used (50% of the total bottom surface area) due to the reduction in available active sites of the catalyst. In case beads were overlapped one over the other (approx 300 beads), the percentage degradation was reduced to around 72%. This may be due to the decrease in the availability of the effective surface area for the catalyst to bind with the pollutant and trapping of the 4-CPA solution in the void spaces.

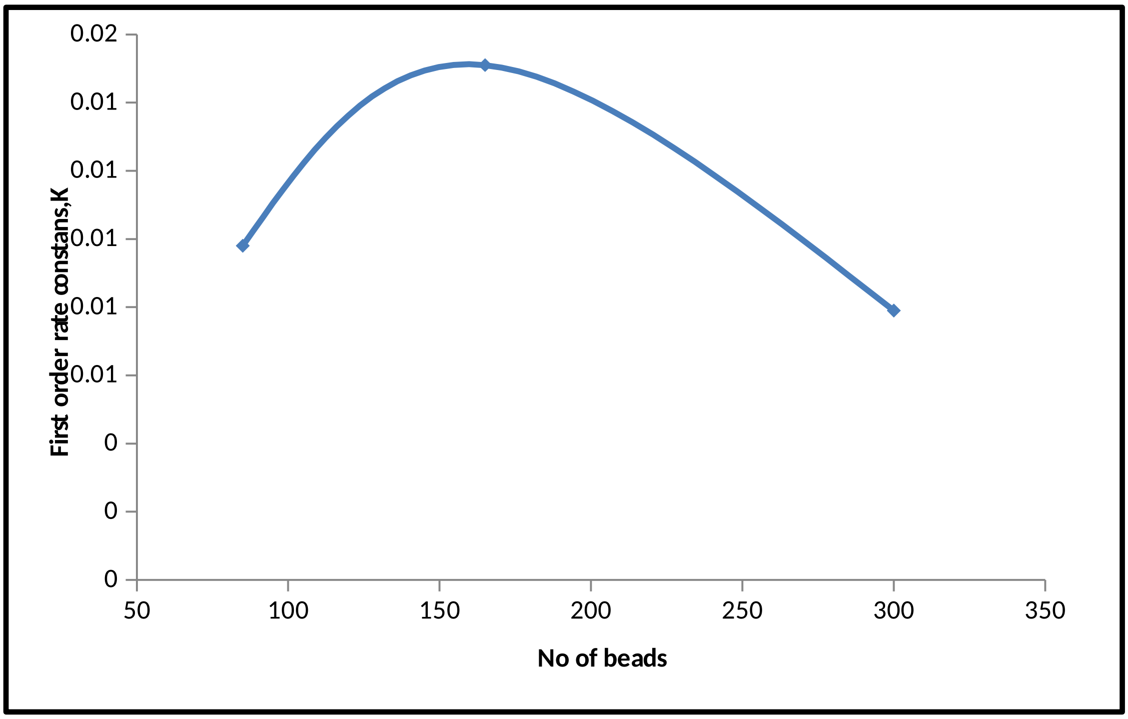


Figure 6.12: plot of first order rate constant Vs No of beads during fixed bed photo catalytic degradation of 4-CPA (C_0= 100 mgL^{-1}, V= 200mL)

6.5 Photo catalytic degradation of 4-CPA using doped catalyst

Experiments were carried out under natural sunlight for degradation studies of the compound (4-CPA) using iron doped catalyst, copper doped catalyst and co-doped catalyst. Initially experiments were performed using 50mg of doped catalyst was added in 50ml solution of 4-CPA.It was observed that doped catalyst proved to be more effective as the degradation was more fast in case of doped catalyst. The possible reason may be that the catalyst became active under visible spectrum of solar radiation as well as it is clear from the values of k below.

	Cu doped (1%)	**Fe doped (1%)**	**Co-doped (1%)**	**TiO_2**
K(first order rate constant)	0.0165	0.0165	0.0174	0.01

Experiments were performed using different concentrations of copper and iron doped catalyst (1%, 2%) and concentrations used for co-doped catalyst were Cu $_{(0.5\%)}$ Fe $_{(0.5\%)}$ and Cu $_{(1\%)}$ Fe $_{(1\%)}$. As it is clear from the figure 6.15 that with co-doped catalyst % degradation has increased to almost 80% within first 50 min as compared to 45% degradation using TiO_2 P-25,65% degradation using copper doped catalyst(fig 6.13) and 55% degradation using iron doped catalyst(fig 6.14) in first 50 min.

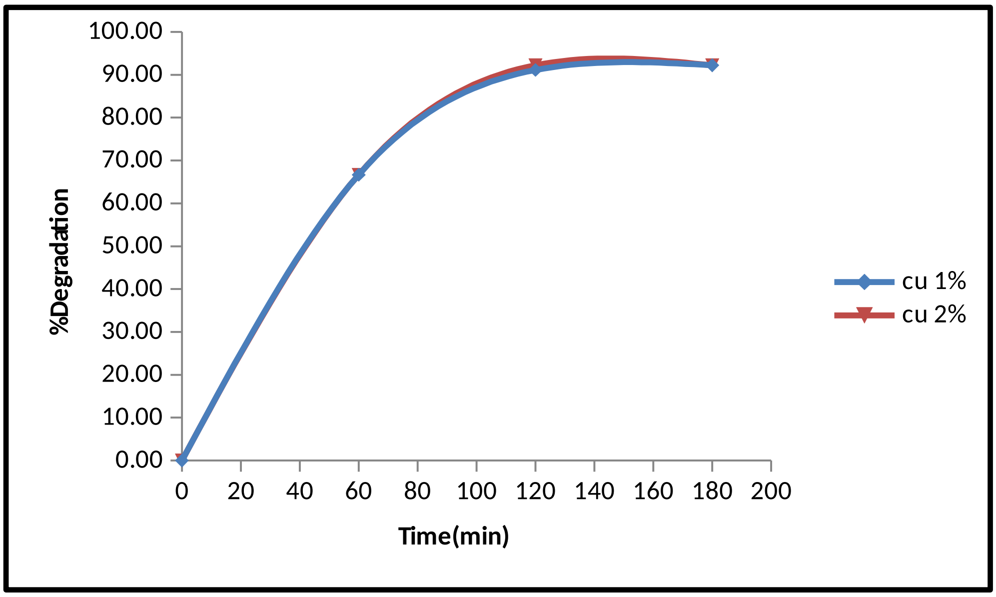


Figure 6.13:% Degradation of 4-CPA using Cu doped catalyst using 1% and 2% concentration of copper

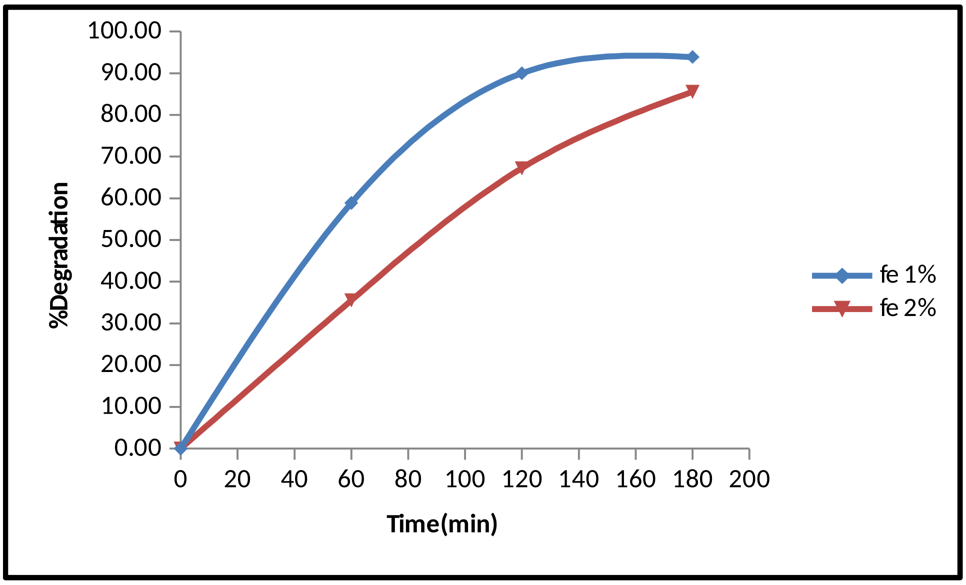


Figure 6.14: %Degradation of 4-CPA using Fe doped catalyst with 1%and 2% concentration of iron

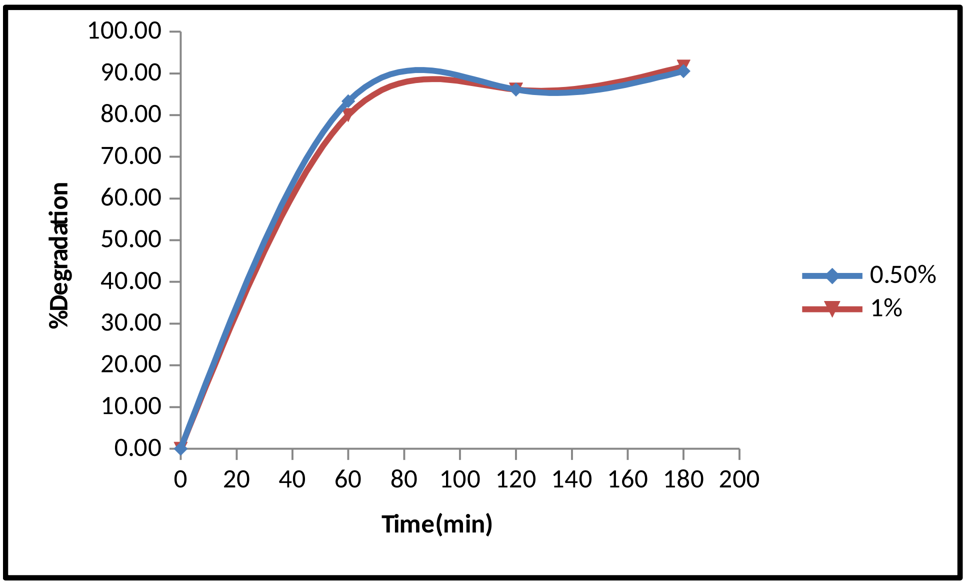


Figure 6.15: %Degradation of 4-CPA using co-doped catalyst (Cu $_{(0.5\%)}$ Fe $_{(0.5\%)}$ and Cu $_{(1\%)}$ Fe $_{(1\%)}$)

It may be concluded that co-doped (iron and copper) catalysts showed best results within 2 hours with almost 80-85% degradation in first hour. This may be because the working range increases using co-doped catalysts.TiO_2 uses 4-6% spectrum of solar radiation but with doping, the working range widens thus leading to more degradation.

CHAPTER 7

CONCLUSION

The present study was undertaken to show the photo catalytic degradation of 4 chloro phenoxy acetic acid (4-CPA) using doped and un-doped TiO_2 in slurry and fixed-bed mode. Parameters like concentration of catalyst, oxidant, pH, UV intensity, A/V ratio play a significant role in the degradation of 4-CPA. The optimized conditions obtained for better degradation of the pesticide are TiO_2 0.625 g L^{-1}, H_2O_2 0.125 mL and C_0 100 mg L^{-1}. $UV/H_2O_2/TiO_2$ photocatalysis resulted in 93.05 % degradation of 4-CPA in aqueous solution. The mineralization of 4-CPA was confirmed by reduction in COD (85.7%) along with the generation of chloride ions (75%), after 2 h of irradiation. For fixed-bed studies, clay beads coated with TiO_2 were used and volume of H_2O_2 was varied and the best result came at 0.7ml of H_2O_2 with 97.16% degradation after 5 h. The durability of beads is usually a major concern for commercial applications and in our study, durability of beads was confirmed by SEM-EDAX analysis which proved the stability of catalyst even after 30th recycle for degrading 4-CPA. Also experiments were performed using doped catalyst with different concentrations of copper and iron (1%, 2%) and concentrations used for co-doped catalyst were $Cu_{(0.5\%)}Fe_{(0.5\%)}$ and with co-doped catalyst % degradation has increased to almost 80% within first 50 min as compared to 45% degradation using TiO_2 P-25,65% degradation using copper doped catalyst and 55% degradation using iron doped catalyst in first 50 min. It may be concluded that co-doped (iron and copper) catalysts showed best results within 2 hours with almost 80-85% degradation in first hour.

To the best of our knowledge, no study has been carried out so far for the degradation of 4-CPA through slurry, fixed-bed and using doped catalyst for photocatalysis. Durability of the supported material to be used for longer period and the choice of supported material are the major concerns to be looked carefully for field scale applications. Also various modifications can be made in doping of the catalyst in terms of type of compound (metal/non-metal) to be doped on TiO_2, different concentrations of the doped compound.

Hence, in the proposed study, efforts have been made to obtain a viable solution to treat wastewater containing these types of pesticide compounds using photocatalysis.

References

1. Aaron, Jacques.j, and Mehmet A. Oturan. "New photochemical and electrochemical methods for the degradation of pesticides in aqueous media. Environmental applications." *Turkish Journal of Chemistry* 25.4 (2001): 509-520.
2. Agarwal, A., Pandey R.S and Sharma B. "Water pollution with special reference to pesticide contamination in india. Scientific research. J." *Water Resour Prot* 2 (2010): 432-448.
3. Balakrishnan.b, Ramesh, Mohamed.K, Meera.S, and Venkatesan.P "Removal of pesticides from wastewater by electrochemical methods–A comparative approach." *Methods* 12.16 (2011): 3-3.
4. Behnajady M. A, Modirshahla N., Hamzavi R., Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst, *Journal of Hazardous Materials*, B133 (2006) 226-232.
5. Burrows, H. D., Santaballa J.A, and Steenken S. "Reaction pathways and mechanisms of photodegradation of pesticides." *Journal of photochemistry and photobiology B: Biology* 67.2 (2002): 71-108.
6. Cao, Yongsong, et al. "Preparation of Ag‐doped TiO_2 nanoparticles for photocatalytic degradation of acetamiprid in water." *Journal of chemical technology and biotechnology* 83.4 (2008): 546-552.
7. Carey, John H., Lawrence.J, and Helle M. Tosine. "Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions."*Bulletin of Environmental Contamination and Toxicology* 16.6 (1976): 697-701.
8. Dalrymple, Omatoyo K., Daniel H. Yeh, and Maya A. Trotz. "Removing pharmaceuticals and endocrine‐disrupting compounds from wastewater by photocatalysis." *Journal of Chemical Technology and Biotechnology* 82.2 (2007): 121-134.
9. Daneshvar, N. "Immobilization of TiO_2 nanopowder on glass beads for the photocatalytic decolorization of an azo dye CI Direct Red 23." *Journal of Environmental Science and Health, Part A* 40.8 (2005): 1605-1617.
10. Davis, Allen P., and Huang C.P. "The removal of substituted phenols by a photocatalytic oxidation process with cadmium sulfide." *Water Research*24.5 (1990): 543-550.
11. Debabrata,C and Dasgupta.S "Visible light induced photocatalytic degradation of organic pollutants." *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 6.2 (2005): 186-205.
12. Doll, Tusnelda E., and Fritz H. Frimmel. "Cross-flow microfiltration with periodical back-washing for photocatalytic degradation of pharmaceutical and diagnostic residues–evaluation of the long-term stability of the photocatalytic activity of TiO_2." *Water research* 39.5 (2005): 847-854.

13. Doll, Tusnelda E., and Fritz H. Frimmel. "Photocatalytic degradation of carbamazepine, clofibric acid and iomeprol with P25 and Hombikat UV100 in the presence of natural organic matter (NOM) and other organic water constituents." *Water Research* 39.2 (2005): 403-411.
14. Doll, Tusnelda E., and Fritz H. Frimmel. "Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water." *Catalysis today* 101.3 (2005): 195-202.
15. Dubey S. K., Kumar A., Srivastava P., & Rajor A., Solar photo-catalytic Treatment of Textile Wastewater for Biodegradability Enhancement, *International Journal of Environmental Engineering*, 1 (2009) 152–164.
16. El Madani, M., "Photocatalytic degradation of diuron in aqueous solution in presence of two industrial titania catalysts, either as suspended powders or deposited on flexible industrial photoresistant papers." *Applied Catalysis B: Environmental* 65.1 (2006): 70-76.
17. Evgenidou E., Fytianos K., & Poulios I., Photocatlytic oxidation of dimethoate in aqueous solutions, Journal *of Photochemistry and Photobiology, A: Chemistry*, 175 (2005) 29–38.
18. Fresno, Fernando, "Photocatalytic degradation of a sulfonylurea herbicide over pure and tin-doped TiO_2 photocatalysts." *Journal of Photochemistry and Photobiology A: Chemistry* 173.1 (2005): 13-20.
19. Galindo, Catherine, Jacques.P, and Kalt.A, "Photooxidation of the phenylazonaphthol AO20 on TiO_2: kinetic and mechanistic investigations."*Chemosphere* 45.6 (2001): 997-1005.
20. Ganesh,B "Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water." *Applied Catalysis B: Environmental* 47.2 (2004): 73-84.
21. Gaya, Ibrahim.U and Abdullah.A.H "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems." *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 9.1 (2008): 1-12.
22. Haarstrick, Andreas, Kut.O.M, and Heinzle.E. "TiO_2-assisted degradation of environmentally relevant organic compounds in wastewater using a novel fluidized bed photoreactor." *Environmental science & technology* 30.3 (1996): 817-824.
23. Hernandez, Rafael,"Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water." *Journal of hazardous materials* 92.1 (2002): 33-50.
24. Herrman J.M. "Heterogeneous photocatalysis: state of the art and present applications in honor of Pr. RL Burwell Jr. (1912–2003), Former Head of Ipatieff Laboratories, Northwestern University, Evanston (Ill)." *Topics in Catalysis* 34.1-4 (2005): 49-65.

25. Hoar S.K., Blair A., Holmes F.F., Boysen C.D., Robel R.J., Hoover R. and Fraumeni J.F. Agricultural herbicide use and risk of lymphoma and soft-tissue sarcoma. *Jama*, *256*(9), (1986)1141-1147.
26. Hoffmann M. R., Martin S. T., Choi W. and Bahnemann D. W., Environmental applications of semiconductor photocatalysis, *Chemical Reviews*, 95 (1995) 69-96.
27. Kim, Kyoung-Hun, and Son-Ki Ihm. "Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review."*Journal of Hazardous Materials* 186.1 (2011): 16-34.
28. Konstantinou, K., and Albanis.T, "Degradation pathways and intermediates of photocatalytic transformation of major pesticide groups in aqueous TiO_2 suspensions using artificial and solar light: A review." *Applied Catalysis B: Environmental* 42 (2003): 319-335.
29. Kositzi M., Antoniadis A., Poulios I., Kiridis I., Malato S., Solar photocatalytic treatment of simulated dyestuff effluents, *Solar Energy*, 77 (2004) 591-600.
30. Leyva, E., "Photodegradation of phenol and 4-chlorophenol by BaO–Li 2 O–TiO_2 catalysts." *Catalysis Today* 40.4 (1998): 367-376.
31. Lhomme, L., Brosillon, and Wolbert.D, "Photocatalytic degradation of pesticides in pure water and a commercial agricultural solution on TiO_2 coated media." *Chemosphere* 70.3 (2008): 381-386.
32. Li, X. Z., and Li.F.B, "Study of Au/Au3+-TiO_2 photocatalysts toward visible photooxidation for water and wastewater treatment." *Environmental science & technology* 35.11 (2001): 2381-2387.
33. Loganathan, Kumaresan,,"The syntheses, characterizations, and photocatalytic activities of silver, platinum, and gold doped TiO_2 nanoparticles." *Environmental Engineering Research* 16.2 (2011): 81-90.
34. Malato S., Blanco J., Maldonado M., Fernandez-Ibanez P., Campos A., Optimising solar photocatalytic mineralisation of pesticides by adding inorganic oxidising species; application to the recycling of pesticide containers, *Applied Catalysis, B: Environmental*, 28 (2000) 163-174.
35. Misra R., Satyanarayan.S, and Potle.N "Treatment of agrochemical/Pesticide Wastewater by Coagulation/Flocculation Process." 82.2 (2007): 121-134.
36. Noorjahan M. "Photocatalytic degradation of H-acid over a novel TiO_2 thin film fixed bed reactor and in aqueous suspensions." *Journal of Photochemistry and Photobiology A: Chemistry* 156.1 (2003): 179-187.
37. Ozer, Ruya R., and Ferry L."Investigation of the photocatalytic activity of TiO_2-polyoxometalate systems." *Environmental science & technology* 35.15 (2001): 3242-3246.

38. Parra S., Stanca S. E., Guasaquillo I. and Thampi K. R., Photocatalytic degradation of atrazine using suspended and supported TiO_2, *Applied Catalysis B: Environmental,* 51 (2004) 107-116.
39. Parra, Sandra, "Photocatalytic degradation of atrazine using suspended and supported TiO_2." *Applied Catalysis B: Environmental* 51.2 (2004): 107-116.
40. Pathak, Kumar.R, and Dikshit A.K, "Various techniques for Atrazine removal." *Int Conf Life Sci Technol*. Vol. 3. 2011.
41. Pérez-Estrada, Leónidas A.,"Photo-Fenton degradation of diclofenac: identification of main intermediates and degradation pathway." *Environmental science & technology* 39.21 (2005): 8300-8306.
42. Poulios I., Micropoulou E., Panou R., Kostopoulou E., Photooxidation of eosin Y in the presence of semiconducting oxides, *Applied Catalysis, B: Environmental*, 41 (2003) 345-355.
43. Pozzo, Roberto L., Baltanas M.A, and Cassano A.E, "Supported titanium oxide as photocatalyst in water decontamination: state of the art."*Catalysis Today* 39.3 (1997): 219-231.
44. Primo, Ana, Corma.A and García H, "Titania supported gold nanoparticles as photocatalyst." *Physical Chemistry Chemical Physics*13.3 (2011): 886-910.
45. Rao, K., Subba V, "Immobilization of TiO_2 on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants." *Applied Catalysis B: Environmental* 46.1 (2003): 77-85.
46. Rao, Neti.N, Chaturvedi.V and Puma G.L, "Novel pebble bed photocatalytic reactor for solar treatment of textile wastewater."*Chemical Engineering Journal* 184 (2012): 90-97.
47. Reddy A.K, "Photocatalytic degradation of isoproturon pesticide on C, N and S doped TiO2." *Journal of Water Resource and Protection* 2010 (2010).
48. Robertson, Peter K.J, "Photocatalytic detoxification of water and air."*Environmental Photochemistry Part II*. Springer Berlin Heidelberg, 2005. 367-423.
49. Sadik, Wagih A., Adel W. Nashed., and Abdel-Ghaffar M., El-Demerdash. "Photodecolourization of ponceau 4R by heterogeneous photocatalysis."*Journal of Photochemistry and Photobiology A: Chemistry* 189.1 (2007): 135-140.
50. Senthilnathan, J., and Philip L, "Photocatalytic degradation of lindane under UV and visible light using N-doped TiO_2." *Chemical engineering journal* 161.1 (2010): 83-92.
51. Singare, P. U., and Patange A.N, "Ion-exchange reaction thermodynamics to study the selectivity behaviour of nuclear and non-nuclear grade anion exchange resins." *International Letters of Chemistry, Physics and Astronomy* 6 (2014).
52. Singh V.K, "Removal of malathion from aqueous solutions and waste water using fly ash." *Journal of Water Resource and Protection* 67 (2010).721-732.

53. Stephan, Brosillon, Ludovic.L and Dominique.W, "Modelling of a falling thin film deposited photocatalytic step reactor for water purification: Pesticide treatment." *Chemical Engineering Journal* 169.1 (2011): 216-225.
54. Subrahmanyam M., "Pumice stone supported titanium dioxide for removal of pathogen in drinking water and recalcitrant in wastewater." *Solar Energy* 82.12 (2008): 1099-1106.
55. Toor P, "Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO_2 in a shallow pond slurry reactor." *Dyes and pigments* 68.1 (2006): 53-60.
56. Verma A, Chhikara I and Dixit D "Photocatalytic treatment of pharmaceutical industry wastewater over TiO_2 using immersion well reactor: synergistic effect coupling with ultrasound." *Desalination and Water Treatment* 52.34-36 (2014): 6591-6597.
57. Verma A,"Heterogeneous photocatalytic degradation of 2-chloro-4-nitrophenol using slurry and fixed bed reactor." *Environmental Progress & Sustainable Energy* 34.2 (2015): 380-386.
58. Verma A., Prakash N.T and Toor A.P, "An efficient TiO_2 coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies." *Chemosphere* 109 (2014): 7-13.
59. Verma A., Prakash N.T and Toor A.P, "Photocatalytic degradation of herbicide isoproturon in TiO_2 aqueous suspensions: Study of reaction intermediates and degradation pathways." *Environmental Progress & Sustainable Energy* 33.2 (2014): 402-409.
60. Verma.A.,"Heterogeneous photocatalytic degradation of 2-chloro-4-nitrophenol using slurry and fixed bed reactor." *Environmental Progress & Sustainable Energy* 34.2 (2015): 380-386.
61. Wang X. H, "Wavelength-sensitive photocatalytic degradation of methyl orange in aqueous suspension over iron (III)-doped TiO_2 nanopowders under UV and visible light irradiation." *The Journal of Physical Chemistry B* 110.13 (2006): 6804-6809.
62. Wissiak, Katarina S., Šket.B, and Vrtačnik M , "Heterogeneous photocatalytic decomposition of halosubstituted benzyl alcohols on semiconductor particles in aqueous media." *ChSemosphere* 41.9 (2000): 1451-1455.
63. Wu, Jeffrey C-S., and Chen C.H, "A visible-light response vanadium-doped titania nanocatalyst by sol–gel method." *Journal of Photochemistry and Photobiology A: Chemistry* 163.3 (2004): 509-515.
64. Yadav P,*Titanium dioxide mediated photocatalytic degradation of chlorpyrifos in Aqueous Phase*. Diss. Thapar University Patiala, 2010.
65. Yin, Hengbo, "Photoreductive dehalogenation of halogenated benzene derivatives using ZnS or CdS nanocrystallites as photocatalysts."*Environmental science & technology* 35.1 (2001): 227-231.
66. Zayani G., Bousselmi L., Mhenni F. and Ghrabi A., Solar photocatalytic degradation of commercial textile azo dyes: Performance of pilot plant scale thin film fixed-bed reactor, *Desalination*, 246 (2009) 344–352.

67. Zhao H., Xu S., Zhong J. and Bao X., Kinetic study on the photocatalytic degradation of pyridine in TiO_2 suspension systems, *Catalysis Today*, 93-95 (2004) 857-861.
68. Zhu, Chunmei, "Photocatalytic degradation of Azo dyes by supported TiO_2+ UV in aqueous solution." *Chemosphere* 41.3 (2000): 303-309.