Degradation of Pesticides in Groundwater by Advanced Oxidation Processes

Thesis

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by

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Certificate

This is to certify that the thesis entitled **"Degradation of Pesticides in Groundwater by Advanced Oxidation Processes"**, submitted by Anoop Verma in the partial fulfilment of the requirements for the award of the degree of Doctoral of Philosophy in the Department of Bio-technology and Environmental Sciences, Thapar University, Patiala, is a record of the candidate's own work carried out by him under our supervision and guidance. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

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Declaration

I hereby declare that the thesis entitled **"Degradation of Pesticides in Groundwater by Advanced Oxidation Processes"** which is being submitted to Department of Biotechnology and Environmental Sciences, Thapar University, Patiala in partial fulfilment of the requirement for the degree of **Doctoral of Philosophy,** has previously not formed the basis for the award of any degree, diploma, associateship, fellowship or any other similar title. It is certified that the thesis is entirely my own and that the idea and references cited herein have been duly acknowledged.

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(ANOOP VERMA)

ABBREVIATIONS

AOP	Advanced Oxidation Processes
APHA	American Public Health Association
NH^{4+}	Ammonium ions
A/V	Area/Volume
BHC	Benzene Haxachloride
BOD	Biochemical Oxygen Demand
BET	Brunauer–Emmett–Teller
CB	Conduction Band
COD	Chemical Oxygen Demand
DDT	Dichlorodiphenyltrichloroethanne
eV	Electron Volt
EDS	Energy-dispersive X-ray Spectroscopy
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
gm	Gram
HPLC	High-performance Liquid chromatography
Hr/ hrs	Hour/ Hours
H_2O_2	Hydrogen Peroxide
OH•	Hydroxyl Radicals
I	Intensity
IPU	Isoproturon
k	First Order Rate Constant
L	Liter
M	Meter

min	Minutes
mg	Milligram
OCPs	Organochlorine Pesticides
Ops	Organophosphate Pesticides
PTC	Parabolic Trough Collector
SEM	Scanning Electron Microscope
SFBBR	Solar Fixed-bed baffled Reactor
TiO_2	Titanium Dioxide
TOC	Total Organic Carbon
UV	Ultra-violet
UV-Vis	Ultraviolet and Visible light
VB	Valance Band
W	Watt

ABSTRACT

Safe and clean drinking water is a right of every human being on this earth. The industrial and agricultural activities have made this precious element unfit for human consumption. Major reasons for water pollution being discharge from different industries and indiscriminate use of pesticide in agricultural fields. Pesticide pollution of surface water and groundwater has been recognized as a major problem in many developing countries because of the persistence of pollutants in aquatic environments. One of the consequences of indiscriminate use of pesticide is the adverse health impact on society in general and vulnerable population like children in particular. Humans are exposed to pesticides found in environmental media (soil, water, air and food) by different routes of exposure such as inhalation, ingestion and dermal contact. Some of the well-known health effects of pesticide exposure include acute poisoning, cancer, neurological effects and reproductive and developmental effects.

Conventional treatment technologies like physico-chemical, biological treatment, air stripping and carbon absorption have limitations as they merely change the phase of the pollutant. Biological methods are incapable especially where the organic pollutants are bio-recalcitrant in nature like pesticides. Thus, incapability of conventional and biological treatment methods for removal of pesticides has substantially increased the concern. Lack of knowledge, repeated and overdose of pesticides has irreversibly damaged our land, air and water bodies, thus has invited many researchers for novel treatment options.

In recent past, advanced oxidation processes (AOPs) have proved their worth for the remediation of contaminated wastewaters containing non- biodegradable organic pollutants. The main mechanism of AOPs is the generation of highly reactive

free radicals like hydroxyl radicals ($OH^{\bullet}$) which are effective in destroying organic chemicals because of their high reactive electrophilic behaviour. The use of advanced oxidation processes (AOPs) such as heterogeneous as well as homogeneous photocatalysis have been the widely studied in the past for the degradation of pesticides. These advanced processes are attractive treatment options as they completely degrade the pesticides without transferring them in other phases unlike other treatments like adsorption and air stripping. TiO_2, now widely accepted photocatalyst, is inexpensive, stable and inert. The mechanism of the heterogeneous photo-oxidation and reduction is well established and discussed extensively in the literature. Hydroxyl radicals ($^{\bullet}OH$) generated are non-selective in nature and they can react without any other additives with a wide range of contaminants whose rate constants are usually in the order of 10^6 to 10^9 mol L^{-1} s^{-1}. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization**.**

A large amount of research has been undertaken in recent past on advanced oxidation processes (AOP) especially heterogeneous photocatalysis for the degradation of toxic compounds. TiO_2 photocatalysis, in slurry form, is gaining more importance in the area of AOP to degrade toxic compounds as it is chemically inert, stable, strong oxidizing power and relatively inexpensive. Main technical limitation of this slurry form is basically separation of catalyst from the slurry and huge cost associated behind effective separation. This is one of the major reasons challenging its commercial applications. This problem can be resolved by immobilizing the catalyst on effective support material. Many studies dedicated to TiO_2 immobilization have been reported over different inert supports like glass beads, pumice stone, wood, plastics etc. In these works, different coating methods, reactor arrangements have been stressed upon from

both engineering and fundamental point of view. But the durability, cost and recyclability of the immobilized system have not been effectively addressed. Moreover, the inertness of support material is also a major concern, which has not been stressed upon.

The work presented in this thesis has been undertaken to study the degradation of herbicide isoproturon and insecticide imidacloprid by photocatalytic oxidation process in slurry and fixed photocatalysis using laboratory and pilot-scale reactors as well. Experiments under solar conditions demonstrated the efficiency of the photocatalytic reactors for field-scale applications.

The study has been presented in five major chapters in the following text. The **first chapter** introduces the origin of the problem and its content, which is subsequently supported by literature review on the pesticides pollution and photocatalytic degradation in **second chapter**. The experimental procedures, reagents and chemicals used and analytical techniques are elaborated in **chapter three**.

Chapter four discusses the study on photocatalytic degradation of herbicide isoproturon and insecticide imidacloprid in slurry and fixed form using laboratory and pilot-scale reactors. Heterogeneous photocatalytic degradation and mineralization of herbicide derivative Isoproturon was investigated in aqueous solutions containing titanium dioxide (**Section 4.3**) at laboratory scale. The degradation rate was found to be strongly dependent on catalyst concentration, initial pH, substrate concentration, intensity of the light (UV) source and area/volume ratio (A/V). The degradation rate was observed to follow first-order kinetics. The degradation was monitored by observing the change in absorption intensity in UV range and through HPLC analysis. Reduction in COD and TOC values along with the generation of ammonium further indicated the mineralization of the herbicide. An attempt was also

made to identify the intermediates (degradation products) through LC-MS analysis. TiO_2 loading 0.5 g L^{-1}, pH 5.0, C_0=25 mg L^{-1} are the optimized conditions for obtaining the better degradation rates. The COD reduction (96%) and TOC reduction (90%) along with ammonium ion generation confirmed the mineralization of the herbicide, isoproturon. The intermediates could be further degraded into different intermediate compounds as evident through HPLC and LC-MS data. The observations, clearly demonstrates that outcome of the study can be suitably utilized for removal of pesticides from water/wastewaters using this technology as pre or post treatment.

Section 4.4 presents the investigation on the fixed-bed photocatalysis at lab-scale for the degradation of herbicide isoproturon. The use of cement beads for the immobilization of TiO_2 has been presented and subsequently tested for the degradation of isoproturon. The immobilized system was effective in degrading and mineralizing the herbicide for continuous thirty cycles without losing its durability. Effect of operating parameters like number of catalyst coatings, bead diameter, UV intensity, calcination temperature etc., were also studied for field scale applications. Catalyst coating was characterized by SEM-EDAX for checking the durability of the catalyst. The degradation rate followed first order kinetics as measured by change in absorption intensity in UV range as well as HPLC analysis. Two rounds of TiO_2 coating on inert cement beads with average diameter 1.5 cm at 25 Wm^{-2} calcined at 400^oC were the optimized conditions for the degradation of herbicide isoproturon. More than 90% TOC and COD reduction along with ammonium ions generation (80%) confirmed the mineralization of isoproturon. Fixed bed baffled reactor (FBBR) studies under solar irradiations using the TiO_2 immobilized beads confirmed 85% degradation after 6h. LC-MS studies confirmed the intermediates formation and their subsequent degradation using immobilized system.

The photocatalytic degradation of insecticide imidacloprid using shallow pond slurry reactor at lab-scale is being described in **section 4.5**. The degradation was studied by varying the operating conditions like catalyst dose, oxidant addition, operating pH, initial concentration, area/volume (A/V) ratio, as in the case of isoproturon (section 4.3) and optimum conditions were determined. The maximum degradation was observed with TiO_2 dose of 1.0 gL^{-1}, pH 6.5, H_2O_2 3.0 gL^{-1} with A/V 1.18 cm^2 mL^{-1}. The 86% COD reduction along with the chloride ions (Cl^{-1}) generation confirmed the mineralization of parent compound during photocatalytic irradiations experiments. In continuation of section 4.4, the photocatalytic degradation of imidacloprid using TiO_2 immobilized on suitable support material is described in **section 4.6.** The TiO_2 immobilized cement beads were used to study degradation of imidacloprid at lab-scale batch reactor. Effect of certain parameters like number of coatings, calcination temperature, exposed area, UV intensity etc. were checked for studying the degradation of imidacloprid. Durability of support was checked by recycling the beads for 20-30 times for imidacloprid degradation.

Authenticity of the lab-scale results can be verified by scaling–up the photocatalytic process to promote the feasibility of photocatalytic water treatment technology at industrial scale in near future. The studies presented in **section 4.7** discussed the scale-up for both slurry and fixed-bed reactor used for the degradation of isoproturon. In scale-up slurry reactor, the study of various parameters has been done like depth of solution to be treated, flow-rate variation for constant area/volume. The parabolic trough concentrator (PTC) was used for the degradation of pesticide solution using immobilized TiO_2 catalyst (cement beads) under concentrated sunlight. Parameters like effect of flow rate of pesticide solution, reusability of coated beads were studied using solar irradiations.

Chapter five summarises that photocatalytic technologies (AOP) have potential for treating the water/wastewater containing biorecalcitrant compounds like pesticides. Experimental results demonstrate the efficacy of both slurry and fixed-bed photocatalysis for the degradation of pesticides.

Successful scale-up studies using slurry batch reactor and fixed-bed reactor (PTC) have shown potential of photocatalytic processes to handle large volume of industrial wastewater.

Even for fixed and slurry TiO_2, the operational costs of these AOPs for total oxidation/degradation of bio-recalcitrant remain relatively very high as compared to biological processes. However, their use as a pre or post treatment option to enhance biodegradability of wastewater containing these bio-recalcitrant compounds can potentially be justified.

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Chapter 1

INTRODUCTION

"Chemicals have replaced bacteria and viruses as the main threat to health. The diseases we're beginning to see as the major causes of death in the latter part of this century and into the 21st century are diseases of chemical origin." -- Dick Irwin, toxicologist at Texas A&M University

Water, undeniably the most valuable natural resource, covers over seventy percent of the earth's surface. Water is central element for all vital, biological, social, recreational and economic processes. On this "blue planet", nearly 30% population has not adequate access to water sources. Adding to this, uncontrolled industrial, agricultural and other recreational activities have degraded the water sources to such an extent that it is posing great threat to water availability.

Pollution of water resources is a serious problem, especially in India, where almost 70% of its surface water resources and significant number of its groundwater reserves are contaminated by biological, organic, inorganic and toxic pollutants. In extreme cases, these water sources have been rendered unsafe for human consumption as well as for other activities, such as irrigation and industrial needs. This ultimately leads to the water quality as its availability will be limited for all the human activities.

Among various persistent water contaminants like pesticides, industrial chemicals, synthetic detergents, and organic solvents; water soluble pesticides are of grave concern because of their easy transport in the environment (Oller et al., 2006). With sufficient water solubility along with combination of chemical stability and resistance to biodegradation, they are capable of penetrating deep into the soil and of

reaching groundwater (Dhaliwal and Singh, 1993). Pesticides from various sources such as industrial effluents, agricultural runoff and chemical spills can significantly contribute to environmental contamination vis-à-vis biomagnification. In developing countries like India, it creates a particular problem where indiscriminate use along with ignorance about the pesticide hazards has led to many causalities (Liu et al., 2005), thus, posing great threat to humans and other organisms (Serpon and Pelizzetti 1989; Carreño et al., 2007). Inhalation, ingestion and dermal contact are different routes of exposure through which humans are exposed to pesticides found in soil, water, air and food. Exposures to these contaminants have created various health effects like acute poisoning, neurological effects, cancer, along with effects on reproduction and development of organisms (Mencher, 1991). Lack of any efficient treatment of water containing these non-biodegradable pesticides worsens the situation. These concerns have prompted researchers to develop novel and effective treatment options.

1.1 Pesticides and their classification

'Pesticide' is a collective term for natural or synthetic substances, that kill or inhibit insects (insecticides), nematodes (nematicides), snails (molluscicides), bacteria (bactericides), fungi (fungicides) and weeds (herbicides) (Table 1). Use of synthetic insecticides has dominated for over half a century as a part of pest-management practices (Farah, 1994).

More than 1100 officially recognized synthetic organic insecticides are commercially available and belong to a vast array of chemical groups.

1.1.1 Organochlorine Pesticides (OCPs)

They (OCPs) are the synthetic organic pesticides basically derived from chlorine. They are broad-spectrum, long residual effect and relatively low toxicity. But, they are hard to degrade in the natural environment due to their stable chemical

configuration (Bouraie et al., 2011; Wang et al., 2013). Long term use in large quantities will easily lead to environmental pollution and accumulation in mammals, resulting in cumulative poisoning or damage. They are, therefore, banned and gradually replaced by other pesticides. DDT, lindane, methoxychlor, pentachlorphenol, camphechlor, endrine, endosulfon and imidacloprid are some of the examples of OC pesticides.

Imidacloprid is classified as a neonicotinoid insecticide in the chloronicotinyl nitroguanidine chemical family. The International Union of Pure and Applied Chemistry (IUPAC) name is 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine. Neonicotinoid insecticides are synthetic derivatives of nicotine, an alkaloid compound found in the leaves of many plants in addition to tobacco (Hayes and laws, 1991; Deepu et al., 2007). Imidacloprid is basically used to control sucking insects like, chewing insects like termites, soil insects, and fleas on pets. In addition, imidacloprid may be applied to structures, crops, soil, and as a seed treatment (Schroeder and Flattum, 1984; Gupta et al., 2002; Fossen, 2006). Although, imidacloprid being pesticide of relatively low toxicity, it has been found to be extremely toxic to non-target insects like bees.

Environmental Protection Agency (EPA) has classified imidacloprid as both a toxicity class II and class III pesticide (on a scale of I to IV, I being the highest toxicity class). Imidacloprid is quickly and nearly completely absorbed from the gastrointestinal tract and eliminated in urine and feaces.

1.1.2. Organophosphate Pesticides (OPs)

They (OPs) are characterized by their multiple functions and the capacity of controlling a broad spectrum of pests. Basically, they are neuronal poisons that are also used as gastro-intestinal toxin as well as but also as contact poisons and fumigants.

These pesticides being biodegradable, cause minimum environmental pollution and have slow pest resistance (Minton and Murray, 1988; Awasthi and Prakash 1997; WHO, 2009). Temephos and Fenitrothion are examples of organophosphate pesticides with subgroups like organo-thiophosphates, derived from phosphoric acid. Disulfon, ethion, malathion, chlorpyrifos, and quanolfos are also some prominent examples.

1.1.3. Carbamates

They basically affect the transmission of nerve signals resulting in the death of the pest by poisoning. They can be used as fumigants, gastro-intestinal and as well as contact poisons (Marer, 1988). They can be easily degraded in a biological environment causing minimum environmental pollution as their molecular structures are more or less similar to that of natural organic substances. Propoxur is an example of carbamate pesticides.

1.1.4. Synthetic Pyrethroids

They are synthesized by mimicing the structure of natural pyrethrins. They have longer residual effects than natural pyrethrins because they are comparatively more stable. Synthetic-pyrethroid pesticides are marginally toxic to mammals besides being highly toxic to insects (Reigart and Roberts, 2013). Allethrin and Permethrin are examples of synthetic-pyrethroid pesticides.

1.1.5. Microbiocides

Microbial insecticides control pests through pathogenic micro-organisms including bacteria, fungus and viruses specific to a group of pests. *Bacillus thuringiensis v. israelensis* (Bti) is an example of microbial insecticides.

1.1.6. Insect Growth Regulators

Insect growth regulators are compounds basically developed by copying insect juvenile hormone. They mainly interfere with the growth and hatching of larvae into adults, and prohibit the growth of the insect by preventing the formation of exoskeleton. Methoprene is an example of insect growth regulators (EPA 2001).

Table 1.1: Characteristics of various pesticides used for different crops

Active ingredient	Chemical class	Toxicological class*	Main use
Chlorpyrifos	Organophosphates	II	Insecticide
Chloropyrifos-methyl	Organophosphates	U	Insecticide
Cyfluthrin	pyrethroids	II	Insecticide
Cypermerthrin	pyrethroids	II	Insecticide
Deltamethrin	Pyrethroids	II	Insecticide
Diazinon	Organophosphates	II	Insecticide
Imidacloprid	Neonicotinoids	II	Insecticide
Dimethoate	Organophosphates	II	Insecticide
Fluometuron	ureas	U	Herbicide
Pendimethalin	Dinitroanilines	III	Herbicide
S-metolachlor	Chloroacetanilides	III	Herbicide
Ethalfluralin	Dinitroanilines	U	Herbicide
Glyphosate	Phosphonoglycines	U	Herbicide
Fluazifop-p-butyl	Aryloxyphenoxypropionic acids	III	Herbicide
Quizalofop-p-ethyl	Aryloxyphenoxypropionic acids	III	Herbicide

*la: extremely hazardous; lb: highly hazardous; II: moderately hazardous; III: slightly hazardous; U: unlikely to present acute hazard in normal use.

1.1.7 Phenyl Urea Herbicides

Isoproturon (IPU) i.e. 3-(4-Isopropylphenyl)-1, 1-dimethylurea is an herbicide belonging to the family of substituted urea and acts particularly after root absorption, either pre-emergence or post emergence. It is mainly applied for control of annual blackgrass, meadowgrass, ryegrass, wild oat, silky bentgrass, and many broadleaf weeds (Srinivasan, 1997). It enters the environment during its application in

agricultural fields, but may also be released/discharged in effluent during manufacture, transportation and storage. Isoproturon can be easily released into aqueous environments because it has a low tendency to adsorb to soils. Its half-life in water and in soils is 30 days and 40 days respectively. This herbicide is not expected to have a high tendency towards bioaccumulation due to its low affinity for organic matter. It is often found in contaminated groundwater, surface water**,** and effluents of wastewater treatment plants (Johnen and Iwan, 1988; Reupert and Ploeger, 1989; Worthing, 1991).

1.2 Mechanism of pesticide action

1.2.1 Neonicotinoids

Neonicotinoids are relatively new type of insecticides, used to control a variety of pests, especially sap-feeding insects, such as aphids, and root-feeding grubs. They are basically systemic pesticides, which are absorbed by plants during their application and move to untreated tissues. Systemic herbicides move to untreated areas of leaves, stems or roots within the plant. They may kill weeds with only partial spray coverage. Unlike contact pesticides, which remain on the surface of the treated foliage, systemics are taken up by the plant and transported to all the tissues (leaves, flowers, roots and stems, as well as pollen and nectar). The insecticide toxin remains active in the plant for many weeks, protecting the crop season-long.

The neonicotinoids affect the central nervous system of insects. They generally bind to receptors of the enzyme nicotinic acetylcholine, causing excitation of the nerves, leading to eventual paralysis and death. Neonics are more persistent as compared to organophosphate and carbamate insecticides, which tend to degrade quite rapidly in the environment. For example, Imidacloprid can leach into groundwater under some conditions because of its persistence for months or years in soil.

1.2.2. Herbicides

A herbicide, known as weed killer, is a type of pesticide used to kill unwanted plants called weeds. They work by killing specific target weeds while leaving the desired crop unharmed. Soil-applied pesticides are applied to the soil and taken up by roots and trans-located inside the plant. Other soil-applied herbicides kill weed seedlings by contact with young shoots or leaves as they break through the soil. There are preplant herbicides are applied before seeding or transplanting into the soil. Pre-mergent herbicides are basically applied to the soil after planting but before emergence of the crop or weed. Trans-located herbicides enter the roots or above ground parts of plants and move within the plants. They are also called systemic herbicides (Kulshrestha and Muckerjee, 1986).

Apart from these, there are fumigants, chemicals which forms a toxic gas that are applied as a solid or liquid. The gas will penetrate cracks and crevices of structures or soil or the spaces between products stored in containers. Eradicant fungicides destroy fungi that have already invaded plants and begun to damage plant tissues. They inhibit metabolic processes of growing fungal organisms. Protectant fungicides prevent fungal infections. They prevent the organisms from entering treated plants or retard fungal growth. They must be applied before the fungi reach the infection stage. After a plant is infected, the fungicide will normally not kill the fungi inside the plant.

1.3 The Indian scenario

The use of synthetic pesticides in crop protection started in 1948-49 with introduction of DDT and BHC. India is one of the few countries that are still in a business of large scale production, use and export of toxic category of pesticides like DDT. Since its formulation, India is only country which has applied more than 100,000 tons of DDT. Even though the use of DDT was banned since 1989 for agricultural use,

India is still a major consumer of DDT. In India, 40% of all the pesticides used belong to organochlroine class of pesticides. Till date, Indian government has banned the use of 30 different types of pesticides, including DDT and refused the registration of 18 other pesticides (Kabra, 2000). Moreover, India also has BIS (Bureau of Indian standard) for pesticides equipments (Mathur, 1999).

The basic source of domestic water supply in India is groundwater and, therefore its purity is main concern at the time of supply to the public. DDT, BHC, carbamate, Endosulfan, imidacloprid, isopruturon etc. are the pesticides generally used in India both in public health and agricultural sectors. Not much importance has been given to the monitoring of pesticides in India. In first ever report on pesticide poisoning in India, over 100 people died in Kerala in the year 1958 due to consumption of wheat flour contaminated with parathion (Karunakaran, 1958). However, presence of some organochlorine pesticides has been reported in some urban water resources and food stuffs (Kannan et al., 1992; Kannan et al., 1997; Senthil et al., 2000). In Gujarat, groundwater contamination has also been reported in some areas near water storage ponds. In these areas, the rain water containing pesticides from agricultural fields, is stored in ponds and during the course of time water (with pesticides) from these ponds enter into the aquifer leading to groundwater contamination by pesticides.

Above all, is the unforgettable industrial accident of the 20th century, **Bhopal tragedy** in 1984. Leakage of 27 tons of methyl isocyanate (MIC), an intermediate for insecticide, caused 20,000 causalities till date and half a million were exposed to deadly gas. Overall, malpractices in pesticides handling and applications have caused grave hazard to environment and human health.

1.3.1 Factors affecting pesticide safety in India

Pesticides are very hazardous class of chemicals, thus must be handled with care. However, there are many factors which makes their safety impossible both in developing as well as developed countries. These factors which are listed below are also our part of our study in which survey was done in related areas of Punjab and Haryana:

- Ignorance about potential hazards of pesticides on health and environment
- Lack of proper dose of pesticide during applications
- Lack of proper training of manpower in terms of pesticide use
- Illiteracy of people handling pesticides, which makes it impossible to read instructions
- Lack of personal safety equipments like gloves, boots, jacket, glasses etc.
- Continuous and indiscriminate use of pesticides
- Faculty equipments for pesticides spraying
- Poor storage facilities for the pesticides
- Lack of knowledge of meteorological data for pesticide spraying
- Inadequate mixing of two pesticides before spraying
- Poor cleaning/washing of used containers leading to bulk disposal of pesticides
- Long hours of spraying
- Easy availability of banned and hazardous pesticides
- Supply of pesticides through untrained dealers
- Lack of medical facilities/first aid at the site of pesticide application

and many more…..

All these listed factors clearly pose a threat to environment from pesticides in India.

1.3.2. Factors affecting the leachability of pesticides

The leachability of the pesticides in groundwater depends on the nature of the soil and the pesticides themselves. The pattern of soil texture, the total organic matter in the soil, pesticide applications, their degradation products are some important factors those control leaching. Soils with fine texture, generally, inhibit leaching of pesticide because of either low vertical permeability or high surface area which enhances adsorption of pesticides. Soil with high organic matter content dissolves the pesticides and decides their transportation into the soil. The properties of soil like pH and temperature are also important factors for the leachability of pesticides (Arias-Estévez et al., 2008). Besides this, the mass flow of water through the soil profile is also an important factor deciding the leaching of pesticides in groundwater.

To meet the food demand of increasing population, use of modern agriculture practices reveal an indiscriminate use of pesticides and fertilizers resulting in contamination of the environment. In India, crop production increased to 100% but the cropping area has increased marginally by 20%. Synthetic pesticides have played a major role in achieving the maximum crop production.

Primarily source of pesticides contamination of surface and ground water is basically runoff from crops and are most prevalent in agricultural areas. Besides agriculture, pesticides are also used on golf courses, along roadsides, forested areas, and in suburban and urban landscape areas. Herbicide and insecticide application to crops has grown to an estimated 660 million pounds of active ingredient in 1993 since World War II. In general, pesticides have the potential to seriously threaten many groundwater supplies throughout the world especially in India.

1.3.3. Environmental health implications

Currently, the pesticide use in India covers about 30% of the cropped area, which has increased steadily from 1950- 51 onwards. The cropped area has increased from 2.4 million hectares (1950) to 137 million hectares (2010) under the chemical pest control. Due to post-green revolution spiraling effects during the 1980s, the total consumption of pesticides was at highest. The declining trend observed later may be attributed to the increased awareness on negative externalities by the farmers or the changes in policies reducing subsidies. Continuous, indiscriminate and non-judicial applications of pesticides contribute to immense deterioration of environment. Investigations have revealed the presence of pesticides and residues in the soil, water, humans, animal and plants. The pesticide particles enter into agricultural products with their concentration some times more than 500 times of maximum permissible limit (Rajendran, 2003). Residual concentration for pesticide exceeds many times for maximum permissible limit in packaged water and soft drinks (Report of CSE-India) according to international norms like European Economic Union.

1.3.4. Scenario in Punjab state of India

One of the worst affected states in India, Punjab, once a land of abundance, affluence, prosperity, is now economically crumbled, ecologically devastated, and fractured part of the globe. Although, the green revolution in Punjab had brought prosperity and development, but has taken away the age-old ecological equilibrium, sustainability, and livelihood. Occupational exposure to pesticides and their poisoning is routine among farmers and farm workers. Data revealed that incidences of cancer, still birth, kidney failure, infertility etc., have been sustainably increasing since past. Most victims are daily wagers and migrant labourers from other parts of the country. Cancer cases are rampant in almost all the villages of Punjab. In a study, the

Community Medicine Department of PGIMER, Chandigarh, has found prevalence of confirmed cancer cases at 103 per lakh Talwandi Sabo, a high figure by any standards (Report of Madhya Pradesh Pollution Control Board). According to reports, the higher number of cancer cases and deaths in Talwandi Sabo is attributed to high usage of pesticides. The story is the same for most of the other villages, where the incidence of cancer is attributed to excessive use of pesticides. The death count starts from the age of 4-5 years and goes up to 60 years or even more in a single village. There are diseases related to reproductive health due to increased dose of pesticides in food chain. Due to this, the numbers of childless couples in villages is also extremely high. Interestingly, a passenger train running between Bhatinda and Bikaner is also known as the 'Cancer Train' as almost 50% of its passengers head to Jaipur for cancer treatment. Laboratory results also reveal that pesticide residues present in leafy vegetables, wheat and rice, fruits, other food items and even mother's milk, thus create health disorders like neural tube defect (NTD) among newborn babies (Report in NYTimes-Asia). There is new insight into the alarming skewed sex-ratio in the state of Punjab and Haryana due to excessive use of pesticides (Report in Tribune-India). According to this report, reproductive toxins chemicals are damaging the reproductive systems of both men and women, thus posing serious threat to human population. These two states, which account for 75% of basmati rice export from India, have recently triggered the controversy over the high residual levels of fungicide (isoprothiolane) in Indian basmati rice. These results were revealed by private laboratory in Hamburg, Germany for the samples of Indian basmati (Report in Tribune-India).

1.4 Ineffective conventional treatment of effluents

Pesticides are globally used chemical substances in agriculture and public health. Because of their persistence in the environment, the use of pesticides has caused many undesirable effects on human health. Their consistent over-use has increased the concentration in the water/wastewater. This needs immediate attention because a direct discharge of these wastewaters have resulted contamination of surface and groundwater. As these contaminants are biorecalcitrant or poorly biodegradable and many are toxic to microorganisms, biological treatment methods are ineffective for the treatment of wastewaters containing these pesticides [Sandermann et al., 1998; Parra et al., 2000; Parra et al., 2002]. Presence of pesticides in drinking water shows ineffectiveness of conventional treatment technologies for removing these pollutants (Meijers et al., 1995; Roche and Prados, 1995; Schuelein et al., 1996). As a result, effective treatment methods are in demand for eliminating these pesticides.

Chemical and biological treatments have their own drawbacks. The production and disposal of large amounts of biological sludge during aerobic treatment is still a major problem, whereas treatment by anaerobic treatment method is not so effective for pollution abatement to the satisfactory level. Other physical and chemical treatments like activated charcoal adsorption; air stripping and coagulation methods simply transfer the pollutants from one medium to another. The activated-sludge process, too, is not effective due to resistance of the pesticides to bacterial degradation. Majority of treatment methods, finally transfer these contaminants either to land, air or water, magnifying the problem of hazardous waste loading on the environment. The lack of any efficient treatment method of pesticides containing water has drawn attention of many researchers towards advanced treatment options. In recent years, developments in water decontamination processes have been oriented towards the oxidation of these bio-

recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade more number of recalcitrant molecules into biodegradable compounds and are called advanced oxidation processes (AOP's).

1.5 Suitability of AOPs as water treatment technology

1.5.1 General Overview

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. These processes are based upon the production of OH* radicals, which are able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions. The hydroxyl radical is having an oxidation potential of 2.8 eV, the second strongest known oxidant after fluorine.

Defined by Glaze et al. (1987), AOP's are water treatment processes that work near ambient temperature and pressure; involve the generation of highly reactive radicals in sufficient quantity to effect oxidation/reduction of bio-recalcitrant compounds. For the degradation of non-biodegradable organic pollutants present in contaminated surface, ground, and wastewaters, these treatment processes are considered as very promising.

1.5.2 Hydroxyl radicals

Hydroxyl radicals ($OH^{\bullet}$) are highly reactive species characterized by a little selectivity of attack. They attack most of the organic molecules with first order kinetics generally in reference to the concentration of the species to be oxidized and concentration of hydroxyl radicals. The main mechanism by which OH radicals attack organic molecules is hydrogen abstraction (Eq. 1.1). This reaction generates organic radicals (Eq. 1.2) which by addition of molecular oxygen yield peroxyl radicals. These

radicals initiate thermal oxidative degradation reactions, thus mineralising the substrate to carbon dioxide, water and inorganic ions.

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \quad (1.1)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow \text{Products and } CO_2 \quad (1.2)$$

Table 1.2: Oxidizing potential for conventional oxidizing agents

Oxidizing agent	Electrochemical oxidation potential (EOP), eV
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen(atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen(molecular)	1.23

1.6 Principle of photocatalysis

Photo catalysis is the acceleration of a degradation process in the presence of a catalyst and light. The photo-catalytic activity (PCA) basically depends on the ability of the catalyst to create electron–hole pairs, which subsequently generate free radicals ($OH^{\bullet}$). AOP can be classified broadly into two type's namely (i) heterogeneous photocatalysis (ii) homogeneous photocatalysis

Different combinations of heterogeneous and homogenous methods which involve the generation of free radicals are: (i) photochemical irradiation with ultraviolet light coupled with powerful oxidizing agents like hydrogen peroxide, ozone and /or a semiconductor; (ii) Fenton and photo-Fenton catalytic processes; (iii) electron beam irradiation technique; and (iv) sonolysis.

The UV spectrum used in above processes is divided into three bands: UV-A (315 to 400 nm), UV-B (280 to 315nm) and UV-C (100 to 280 nm). UV-A and UV-C bands are generally used in environmental applications. UV-A radiations are referred to as long wavelength radiations or black light and UV-C are referred to as short wave radiations.

1.6.1 Homogenous photocatalysis

In homogenous photocatalysis, the reaction takes place in similar or homogenous phases like liquid – liquid phases examples are dye with soluble metal catalyst. Discovered by H.J. Fenton in 1890's (Fenton, 1894), it remains one of the most reliable AOP for its ability to degrade high loading of organic compounds. In homogenous photocatalysis, a powerful UV lamp is used to illuminate the contaminated water in the presence of Fe^{3+}, O_3 or H_2O_2 which act as a catalyst and the reaction takes place in the bulk solution. The Fenton reaction can be outlined as follows:

$$Mn^{2+} + H_2O_2 \rightarrow M^{(n+1)} + OH^{*} + OH^{-}$$

Where, M is a transition metal as Fe or Cu.

In the absence of light and complexing ligands other than water, the most accepted mechanism of H_2O_2 decomposition in acid homogeneous aqueous solution, involves the formation of hydroxyl-peroxyl (HO_2*) and hydroxyl radicals HO*.

The metal regeneration can follow different paths. For Fe^{2+}, the most accepted scheme is described in the following equations.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{*} + OH^{-} \quad (1.3)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH^{*} + OH^{-} \quad (1.4)$$

$$Fe^{2+} + HO^{*} \rightarrow Fe^{2+} + OH^{*} \quad (1.5)$$

$$OH^{*} + H_2O_2 \rightarrow HO_2^{*} + H_2O \quad (1.6)$$

$$Fe^{3+} + HO_2^{*} \rightarrow Fe^{2+} + O_2 + OH^{+} \quad (1.7)$$

$$Fe^{3+} + O_2^{*} \rightarrow Fe^{3+} + O_2 \quad (1.8)$$

$$Fe^{2+} + HO^{*} \rightarrow Fe^{3+} + O_2H^{-} \quad (1.9)$$

Fenton reaction rates are strongly increased by irradiation with UV/visible light (Arslan and Balcioglu, 2000). During the reaction, Fe^{2+} ions are consumed along with the accumulation of Fe^{3+} in the system and the reaction practically stops, the proposed mechanism being photochemical regeneration of ferrous ions (Fe^{2+}) by photoreduction of ferric ions (Fe^{3+}). The new generated Fe^{2+} ion reacts with H_2O_2 generating a subsequent HO* radical and ferric ion, and the cycle continues.

1.6.2 Heterogeneous photocatalysis

It can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pair by suitable light on the surface of the solid semiconductor materials. Heterogeneous photocatalysis using semiconductor oxides are gaining more importance, has demonstrated to be very efficient to degrade pollutants either in gas or in liquid phase (Augugliaro et al., 2006).

Photocatalytic degradation of organic compounds is based on semiconductor photochemistry. The most effective and commonly photocatalyst for this purpose is titanium dioxide (TiO_2). TiO_2 is biologically and chemically inert material, commonly used as constituent of toothpastes, pharmaceuticals, and many cosmetics. The valence

band (VB) and conduction band (CB) energies of the TiO_2 are reported to be +3.1 and -0.1 volts, respectively, which makes its band gap energy to be 3.2 eV and therefore absorbs in the near UV light (<387 nm). Other photocatalyst like ZnO can be a suitable alternative to TiO_2, but it dissolves in acidic solutions and therefore have limited technical applications. Although other semiconductor particles like CdS or GaP can absorb larger fractions of the solar spectrum than TiO_2, unfortunately, such catalysts are susceptible to degradation during the repeated catalytic cycles in heterogeneous photocatalysis.

1.6.3 Mechanism of TiO_2

An electron/hole pair is produced on the semiconductor surface, when it is illuminated by UV radiation with a wavelength < 387.5 nm sufficient to displace electrons from the valence band of the catalyst (Eq. (i)). The electron/hole pair would lead to series of oxidation and reduction reactions in aqueous solution ultimately degrading the target compound (Fig. 1.1). Oxidation and reduction reactions may proceed simultaneously in the system and which mechanism dominates depends on the chemical and adsorption properties of the pollutant. The main advantage of photocatalysis is that there is no further requirement for secondary disposal methods (Gogate and Pandit, 2004a).

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^- + h^+) \qquad (1.10)$$

Two oxidation reactions have been experimentally observed on TiO_2 surface:

Electron transfer from adsorbed substrate (organic pollutants),

$$TiO_2\,(h^+) + RX_{ad} \rightarrow TiO_2 + RX_{ad}^{\bullet +} \qquad (1.11)$$

Electron transfer from adsorbed solvent molecule

$$TiO_2\,(h^+) + H_2O_{ad} \rightarrow TiO_2 + HO_{ad}^{\bullet} + H^+ \qquad (1.12)$$

$$TiO_2\,(h^+) + OH_{ad}^- \rightarrow TiO_2 + HO_{ad}^{\bullet} \qquad (1.13)$$

Due to high concentration of H_2O molecules more HO^- radicals adsorbed at the particle surface, thus reactions (iii and iv) appears to be of greater importance in oxidative degradation processes. Molecular oxygen is responsible for accepting species in the electron- transfer reaction from the conduction band of the photocatalyst to oxygen.

$$TiO_2\,(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \qquad (1.14)$$

The addition of electron acceptors like (H_2O_2) can considerably enhances the rate of photodegradation (iv),

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + HO^{\bullet} + OH^- \qquad (1.15)$$

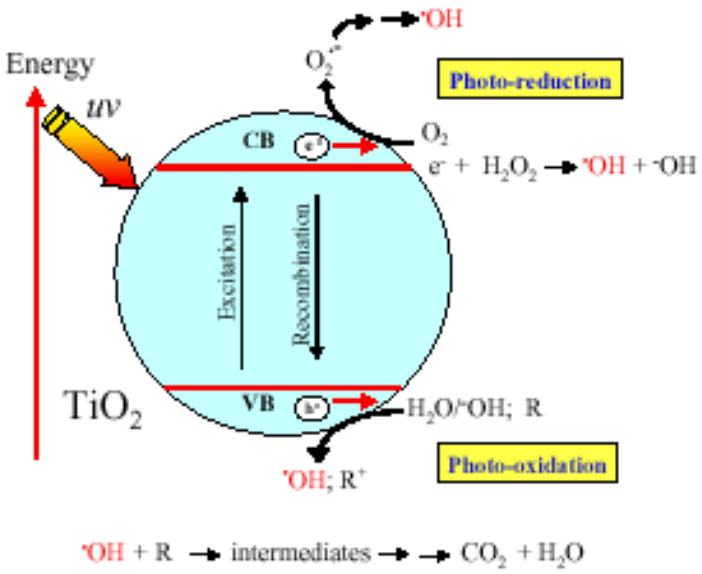


Figure 1.1: TiO_2 semiconductor photocatalysis; Scheme showing photochemical events that might be taking place on an irradiated semiconductor particle (Fujishima et al., 2000)

UV/TiO_2 treatment process has proved to have good potential in field of wastewater treatment as a large number of bio-recalcitrant compounds dissolved or dispersed in water can be completely mineralized. Available at modest price with high rate of reaction, catalyst can be effectively recycled. Surface modifications of TiO_2 can relatively improve its absorption cross-section e.g. by transition metal ion doping.

The only hurdle for its field application is separation of catalyst from the slurry which involves expensive filtration processes to separate the catalyst. The catalyst immobilization on solid support can solve this separation problem, where TiO_2 is fixed on suitable support by coating with a TiO_2 solution.

1.6.4 Fixed bed photocatalysis

TiO_2 photocatalysis, in slurry-mode, has proven to very efficient treatment technology for the removal of contaminants with excellent fluid to catalyst mass transfer and low-pressure drop through the reactor. As the TiO_2 particles are submicron- sized, cost-effective efficient separation is not possible. Main technical limitation of this slurry form is the separation of catalyst from the slurry and huge cost associated behind effective separation. This is one of the major reasons challenging its commercial applications. This problem can be solved by immobilizing the catalyst on suitable support material.

Since 1993, the idea of fixing the photocatalyst on an inert support has begun to be widely accepted and many significant studies have been reported on the anchoring of the photocatalyst particles onto different supports that are readily removable (Parra et al., 2002; Daneshvar et al., 2005; Mahmoodi et al., 2006; Sharma et al., 2008a, 2008b). Various supports have been tested for their efficacy such as glass, polymer, silica gel, metal, thin films, ceramics, zeolite, alumina clays, fibres, cellulose, activated carbon, reactor walls and others (Daneshvar et al., 2005; Parra et al., 2004). But the durability as well as recyclability of the immobilized system remained always a big challenge for the field-scale applications. Moreover, the inertness of support material is also a major concern, which has not been stressed upon.

1.6.5 Solar photocatalytic reactors

The reactors used for the solar photocatalytic treatment are categorized as follows:

i. Concentrating reactors and ii. Non-concentrating reactors

Concentrating reactors

These reactors are based on the focus line parabolic trough concentrators (PTC) which make use of direct solar radiation (Fig. 1.2). All the photochemical treatment processes basically depend on the collection of only high energy short wavelength photons (<365 nm) to promote photochemical reactions. These reactors are based on the collection of large quantities of photons of all wavelengths to initiate the reactions along with an additional advantage; the thermal energy collected from the concentrated radiation could simultaneously be used for other applications (Parra et al., 2001; Momani et al., 2007). The main drawbacks for these collectors are that they use only direct radiations and have low optical and quantum efficiencies, resulting in a low reaction rate constants dependence on the intensity (I) of UV radiation i.e., $k \propto I^{1/2}$

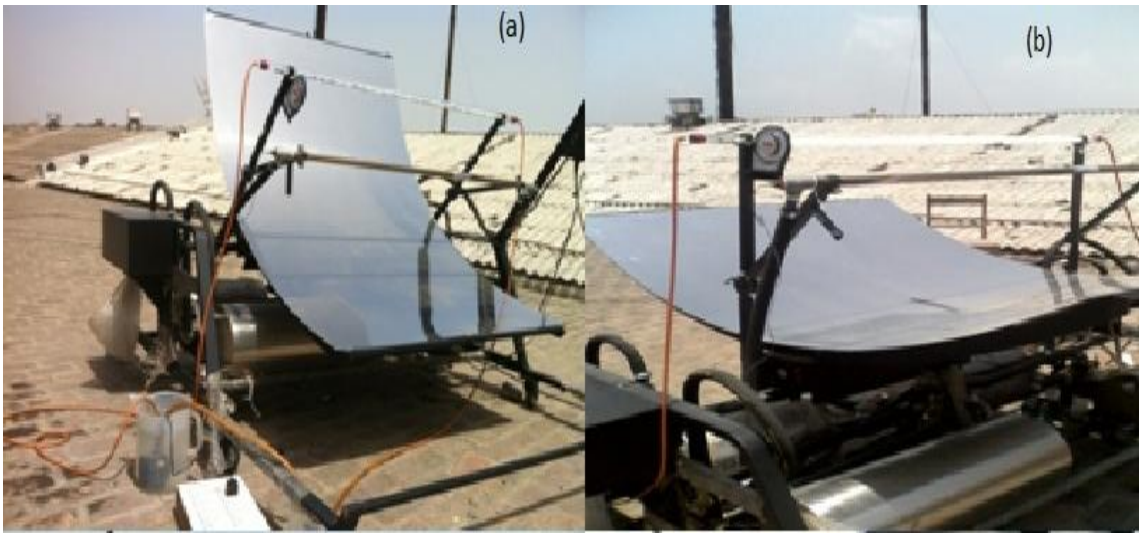


Figure1.2: Concentrated type parabolic trough collector at different angles

Non-concentrating reactors

Non-concentrating solar collectors are static as shown in figure 1.3 and non-solar-tracking. Their main advantage is their simplicity and low cost due to their simple structure and design. Usually, they are flat plates, often aimed at the sun at a specific tilt, depending on the geographic location.

Main disadvantage of these reactors is the requirement of larger reactor area. Different designs of non-concentrating solar reactors have been proposed like flat plate, shallow solar ponds, tubular and falling film.

Shallow-pond type non-concentrated reactors can be constructed on-site especially for industrial treatment (Toor et al., 2005). Ponds used for biological treatment of wastewater in industry can be used as shallow solar ponds, thus can serve best option for a combined solar/ biological treatment of wastewater.

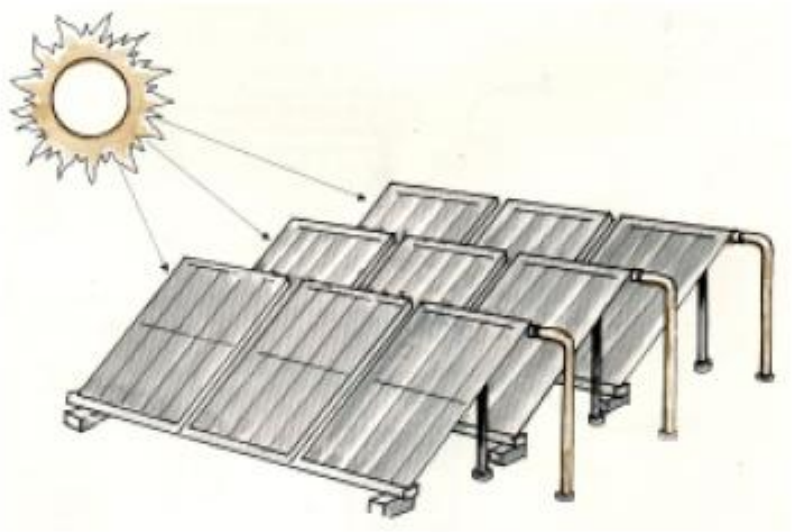


Fig: 1.3. Non-concentrating solar collectors (Parra et al., 2002)

Thus, these reactors have the best chance of commercialization for wastewater treatment in industries such as textiles, pharmaceuticals, pulp and paper and chemicals.

For shallow pond type reactor, the intensity dependence of the reaction rate constant is given by: $k/ko = m [I(A/V) /I_o(A/V)_o]^n$

where 'm' and 'n' are empirical constants, A is the aperture and V is the volume irradiated (Toor et al., 2007).

The study was thus, focused on photodegradation of pesticides found in groundwater using slurry and fixed bed reactor both at lab as well as pilot-scale reactors. After intensive field survey, two pesticides were selected namely, Isoproturon and Imidacloprid, for photodegradation studies. These pesticides were intensively used throughout the year on wheat and paddy crops. Detailed study have been undertaken to study the effect of various operating parameters like pH, substrate and catalyst concentration along with variation in intensity of UV irradiations as well as area/volume (A/V) is also studied for the practical applications both in slurry and fixed bed conditions. An attempt has been made to identify the intermediate products through LC-MS analysis along with the mineralization studies.

Chapter 2

REVIEW OF LITERATURE

2.1 Overview

Nowadays, environmental issues across India are extensively highlighting adverse effects of excessive use of pesticides on living beings. Application of synthetic pesticides to the agricultural fields indiscriminately damages environment as well as affects health and development. Although, pesticides controlled insect and pests diseases and significantly increased the agricultural production, but their extensive use has resulted in degradation of environment and long term negative impacts on the living systems. Human health is threatened by widespread intensive use of pesticides and their high concentrations in environment cause various fatal diseases like cancer, skin disorders, genetic aberrations, neurological disorders and reproductive issues. Due to the wide range of categories of pesticides, most of the studies very often, concentrate on a broadly defined category (Rajendran, 2003). They are the second largest contaminants in drinking water and hence pose potential health hazards towards animals and humans.

Depending on the usage, pesticides are classified into herbicides, insecticides, micro-biocides, fungicides, nematicides, etc. Lack of understanding of safety practices during pesticide use and false beliefs about the requirement of protective equipment has seriously affect farmers' abilities to protect themselves.

Factors governing the potential for groundwater contamination by pesticides include: properties of the soil, hydraulic loading on the soil, properties of the pesticides and crop management practices. Half-life, soil sorption coefficient, vapour pressure and water solubility are key properties of a pesticide that can be used to predict its

environmental fate. In assessing such risks, it is important to assess the synergistic effect of chemicals from a public health perspective (Hughes and Wood, 2002). Three million cases of pesticide poisoning, about 220,000 of which are fatal, occur world-wide every year (Paunero et al., 2009; Raipulis et al., 2009).

Most of the herbicides are applied by ground applications (Kawata, 2009). These chemicals have been detected in a number of water samples including sewage flows, ground and surface water, with concentrations usually ranging from traces to ppb levels. The binding of pesticide to soil, in most cases, is considered weak and penetrates easily through the ground and into the groundwater (Aharonson et al., 1987; Worthing, 1988; Chiron et al., 2000; Stackelberg et al., 2004; Youbin et al., 2010). With their excess usage, there have been numerous detections of pesticides in ground water, surface water (Younes and Galal, 2000). Imidacloprid detections have been reported in both ground water and surface water. A ground water monitoring project conducted by Bayer Corporation (1998) on Long Island, NY, detected imidacloprid in a single agricultural well at concentrations ranging from less than 0.1 ppb to 1.0 ppb over a five month sampling period; the well was located in a sandy loam soil with a water table at 18 feet. Starner and Goh (2012) detected imidacloprid in 89% of the water samples taken from rivers, creeks and drains in California with 19% of samples exceeding the US Environmental Protection Agency (EPA) guideline concentration of 1.05 ppb. Concentrations of up to 200 ppb in groundwater, streams and ditches of the Netherlands have been reported (Van Dijk et al., 2009).

Discharges from production plants along with diffuse agricultural sources are main sources for raw waters contamination with pesticides (Cavalier et al., 1991). In Germany, concentrations of between 0.1 and 0.125 µg/litre have been recorded in surface water (Reupert and Ploeger, 1989). In groundwater, it has been detected at

concentrations of between 0.05 and 0.1 µg/litre (Johnen and Iwan, 1988). Levels above 0.1 µg/litre have occasionally been detected in drinking-water (DoE Reference: WS/45/1/1).

Various reports of poisoning due to pesticides in India came from Kerala, Andhra Pradesh, Punjab and other states. Although normal sewage can be treated in conventional biological and chemical treatment plants, highly toxic anthropogenic compounds cannot be treated the same way. Among the various toxic organic compounds dissolved in water are the pesticides which, through their tremendous use, have become increasingly present in water. Thus, incapability of conventional (Meijers et al., 1995; Roche and Prados, 1995; Schuelein et al., 1996) and biological (Sandermann et al., 1998; Parra et al., 2000; Parra et al., 2002) treatment methods for removal of pesticides has substantially increased the volume of concern. Lack of knowledge, repeated and overdose of pesticides has irreversibly damaged our land, air and water bodies. Most of the pollutants are resistant to conventional chemical treatment methods such as coagulation, activated carbon adsorption, etc. Also, the biological treatment is considered as the typical process for natural decontamination. Unfortunately, all organic pollutants are not biodegradable and there is a class of products noted as bio-recalcitrant organic compounds. As a result, the use of alternative treatment technologies that aim to transform them into their biodegraded form is a matter of great concern.

2.2 Advanced Oxidation Technology

Photocatalysis is a rapidly expanding technology for wastewater treatment. With growing incapability of conventional treatment methods, the photocatalytic detoxification has emerged as an alternative method for cleaning up of polluted water and widely discussed in the scientific literature (Carey et al., 1976). Fujishima et al.

(1999) has reviewed the applications of photocatalytic degradation and chemical effects of various variables on the rate of degradation of different pollutants. A growing interest in the purification of water by semiconductor photocatalysis especially in the removal of toxic organic pollutants is evident by the ever-increasing number of studies in this area (Inel and Okte, 1996; Mathews, 1988). Advanced oxidation processes (AOPs) with the capability of exploiting the high reactivity of hydroxyl radicals in driving oxidation have emerged a promising technology for the treatment of wastewaters containing refractory organic compounds. Several technologies like Fenton, photo-Fenton, cavitation, ozonation, photocatalysis, etc. are included in the AOPs and their main difference is the source of radicals (Gogate et al., 2004a).

AOPs can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms leading to the destruction of the target pollutant. The main mechanism of AOPs function is the production of highly reactive free radicals. Hydroxyl radicals (HO•) destroy organic chemicals as they are reactive electrophiles (electron preferring) that react rapidly and non-selectively with almost all electron-rich organic compounds (Stasinakis, 2008).

The hydroxyl radicals have oxidation potential of 2.33 eV and they show better oxidation reaction rate as compared to usual oxidants such as H_2O_2 or $KMnO_4$ (Gogate and Pandit, 2004b). They have the capability to attack complex compounds by hydrogen abstraction, radical addition and electron transfer. The hydroxyl radicals reacts with the dissolved constituents, initiating a series of oxidants reactions until the constituent are completely mineralized. Advanced oxidation processes differ from the other treatment process as wastewater compounds are degraded rather than

concentrated or transfer into diffused phase. Because secondary waste materials are not generated, and there is no need to dispose of materials**.**

They use strong oxidizing radicals (e.g. H_2O_2, O_3) with the help of catalysts (e.g. transition metal ions) and UV radiations. Scopus database consists of more than 1000 research papers published for the applications of these methods in wastewater treatment during the last decade.

2.3 Heterogeneous catalysis

In this process, titanium peroxide semiconductor generates OH radicals in the presence of UV radiations (Crittenden et al., 2005) in aqueous phase. This process is operated at ambient conditions. There is a possibility of using solar irradiation and no mass transfer limitations exist when nano-particles are used as photocatalyst (Kositzi et al., 2004; Radjenovic et al., 2009). TiO_2 has the capacity for oxidation of a wide range of complex chemical compounds into simple compounds such as CO_2 and H_2O (Chatterjee and Dasgupta, 2005; Momani, 2006).

The critical factors affecting this photocatalytic process are: initial organic load, amount of catalyst, reactor's design, solution's pH, temperature, light intensity, UV irradiation time and presence of ionic species. The use of high amounts of catalyst may decrease the amount of energy being transferred because of opacity caused by catalyst particles (Gogate and Pandit, 2004a). Uniform irradiation of the catalyst surface has to be achieved during the reactor design (Herrmann, 1999; Ray, 1999). The pH of the solution has an important effect on photocatalytic oxidation rates. Reaction rates increase at lower pH under acidic conditions (Andreozzi et al., 2000). Whereas, pollutants which are degraded under alkaline conditions showed increased reaction rates (Choi and Hoffmann, 1997). Ionic species affect the treatment process via

adsorption of the pollutants, reaction with hydroxyl radicals and absorption of UV light.

Photocatalytic degradation has been used to treat olive-oil mill wastewater which removed almost 22% and 94% of COD and phenols respectively (Vigo and Cagliari, 1999; Chatzisymeon et al., 2008). The heterogeneous photocatalysis was also used in order to determine the oxidation rate of phenol present in wastewater and to analyze the effects of initial phenol concentration, amount of catalyst, light intensity and solution's pH (Laoufi et al., 2008). The 99% degradation of the target compound was achieved after 4 hours of irradiation.

The use of AOPs for wastewater treatment has been covered extensively in recent past (Chiron et al., 2000; Esplugas et al., 2002) and concluded that artificial UV lamps are expensive. Therefore, research in this area focusing more and more on using solar radiations for degrading bio-recalcitrant compounds. TiO_2-assisted photocatalysis of pollutants using sunlight proved to be an effective and economically viable process which replaced artificial light sources which are costly and hazardous (Malato et al., 2002; Muruganandham and Swaminathan, 2004).

2.4 Degradation of Pesticides using AOP

As discussed, there are growing concerns of high level of pesticides in groundwater and their subsequent inclusion in food chain. Many researchers have shown that AOP's have potential to degrade almost all class of pesticides into non-toxic products like carbon dioxide, water and some simple acids. The photocatalytic degradation of herbicide, Paraquat (1, l'-dimethyl-4, 4'-bipyridinium dichloride) with UV light over titanium oxide was investigated by Leyva et al. (1998). Experimental results have confirmed that Paraquat is slowly degraded by direct photolysis in the presence of dissolved oxygen. Addition of TiO_2 to the reaction system substantially

increases the initial rate of reaction and the overall conversion of Paraquat. Complete photocatalytic degradation of Paraquat at high pH values was found to occur in less than three hours of reaction. Zhu et al. (2007) studied the photocatalytic degradation of pyridaben under UV irradiation in acetonitrile/water solution containing TiO_2 particles. The primary degradation of the pollutant followed the Langmuir–Hinshelwood model with kinetic constant *k*, 4.3×10^{-5} mol L^{-1} min^{-1} and equilibrium adsorption constant *K*, 3.1×10^{3} L mol^{-1}. Eight kinds of degradation products (DPs) were identified by GC–MS in the process of reaction and some of them were further confirmed by matching with authentic standards and synthesized compounds.

Five carbamate pesticides were degraded photo catalytically on TiO_2. The comparison of their disappearance rates showed that the degradation rate is governed predominantly by their adorability to TiO_2, and followed Hammett's law in a different manner from ordinary electrophilic reaction. Successive hydroxylation of aromatic ring was suggested, and polyhydroxylation is considered to lead to the opening of the aromatic ring to form oxygenated aliphatic intermediates. By-products were subsequently degraded during further photocatalytic treatment. Several studies (Muneer and Bahneman, 2002; Evgenidou et al., 2007) have reported the photocatalytic degradation of various kind of pesticides using TiO_2 and effect of various parameters like catalyst dose, operating pH, oxidant addition have been discussed.

The technical feasibility and performance of photo catalytic degradation of four water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) have been studied by Malato et al. (2002) at pilot scale in two well-defined systems yiz., heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton. The photocatalytic system and experimental conditions allowed disappearance of pesticide and degree of mineralisation achieved was compared in the

two photocatalytic systems. Total disappearance of the parent compounds and 90% mineralisation have been attained with all pesticides tested, methomyl being the most difficult to be degraded with both treatments. Bandala et al. (2002) used concentrated and non-concentrated solar radiation for the photocatalytic degradation of the pesticide Aldrin in aqueous suspensions. In these experiments, the effects of catalyst concentration, oxidant agent concentration, and solar irradiation were tested. In experiments without irradiation, strong adsorption of the pesticide over titanium dioxide was observed in the first few minutes of contact in the presence of titanium dioxide (TiO_2).

Titanium dioxide photocatalysis and photo-Fenton were applied to the treatment of several different pesticides considered priority substances (PS) by the European Commission dissolved in water at concentrations used in the fields or at maximum water solubility. Alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol alone and as a mixture was treated by using new twin compound parabolic collector (CPC) pilot plants driven by solar energy (Maldonado et al., 2007). Decreasing DOC concentrations are representative of the oxidative reactions that occur in the experimental solution during the photocatalytic treatment. Photo-Fenton treatment was found to be shorter than TiO_2 and more appropriate for these compounds and mixtures of them. Intermediates formed during the photodegradation are of main concern because they would really determine the complete mineralization of the pesticides under consideration. The photocatalytic degradation of triazophos in aqueous TiO_2 suspension has been studied in a photoreactor operating with simulated solar radiation. The decrease in triazophos concentration followed first-order kinetics with a half-life of 4.76 ± 0.42 h using TiO_2 suspension. Seventeen degradation products were identified using HPLC-UV, HPLC/MS/MS, GC/MS/MS and IC, by comparing

retention times and spectra with commercially available authentic standards (Aungpradit et al., 2007). The commercially formulated Pirimiphos-methyl, PMM was also degraded, but required a longer time for total mineralization as compared to the technical grade, because of either a stabilization effect due to the formulating agents and/or of a competition of these organic agents for degradation. Heteroatoms (P, S, N) were mineralized into phosphate, sulfate and nitrate anions, respectively (Herrmann et al., 1999). Several others reported the complete mechanism/ pathway of the pesticide/pollutants degradation using AOP using detail analytical studies of the intermediates (Herrmann, 1999; Doll and Frimmel, 2005). Kinetic model using Langmuir-Hinshelwood (L-H) were reported by various researchers for designing, scale-up and optimization of photocatalytic reactions (Percherancier et al., 1995; Bayarri et al., 2005; Gora et al., 2006; Toor et al., 2006).

The photocatalytic oxidation of the herbicides isoproturon, simazine and propazine over irradiated TiO_2 suspensions was studied in single-component and in multicomponent systems using the initial herbicide concentration ranged from 70 μg L^{-1} to 3 mg L^{-1} in order to approach typical concentrations found in contaminated ground and surface waters. The time-dependent degradation profiles of each herbicide were successfully modelled using an approximation of the Langmuir–Hinshelwood (L–H) rate equation, which takes into account the direct effect of the intermediate reaction products (Gora et al. 2006).

Reviews are available in literature relating the photocatalytic activity of TiO_2 toward the degradation of organic compounds in aqueous solutions at low concentrations. The photocatalytic activity of both polycrystalline samples and thin films can be related to the method of preparation of the catalyst. The increase in the

catalytic activity of TiO_2 when certain metals such as silver, gold, and palladium are deposited on the surface has also been discussed (Chatterjee et al., 2006; Anpo, 2000).

2.5 Coupled Advanced Oxidation Processes

Coupling advanced oxidation process (AOPs) with biological systems for wastewater treatment confirms the beneficial effects of such two-steps treatment at lab scale (Marco et al., 1997). Biological treatment is now-a-days considered to be best among the available technologies for wastewater treatment (Sarria et al., 2002) but the degradation of toxic, stable and recalcitrant pollutants require advanced oxidation processes. The strategy to develop this system implicates the choice of the most appropriate solar collector and the most efficient AOP, the optimization of this AOP, the choice of the biological oxidation system, the monitoring of the chemical and biological characteristics of photo-treated solutions and the evaluation of the performances of the coupled solar-biological flow system (Munoz et al., 2006; Dubey et al., 2009; Oller et al., 2007).

A combined solar photocatalytic and biological treatment systems (Bandra et al., 1997; Parra et al., 2000; Kuburovica et al., 2007) as well as coupled solar photo Fenton and biological treatment (Lapertot et al., 2007) has been recently reported for complete minerlization of solution of mixed pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon) employing photocatalytic/ photo-Fenton as a preliminary step before biotreatment. Photo-Fenton degradation is an important sub-process in the integrated photobiological process for removal of biorecalcitrant chemicals. Shortening the photo-Fenton treatment time has a critical impact on the economical feasibility of the integrated process.

2.6 Fixed-bed Photocatalysis

Heterogeneous photocatalysis with titanium dioxide as a semiconductor has proven to be an efficient process for elimination of different types of pesticides, dyes, organic chemicals, industrial effluents, landfill leachates and pathogens from drinking water as discussed above. Mostly UV/TiO_2 systems have been employed in suspension form and are operated in batch mode. But, most obvious problem during suspension form is catalyst filtration, thus raising concerns about its industrial applications. As TiO_2 is non-toxic, cheap and can be supported on suitable materials like glass, quartz , silica, activated carbon, fibre glass cloth, zeolites, stainless steel, polythene film and pumice stone. Thus, photocatalytic treatment and degradation has been reported using fixed/immobilized catalyst on some inert supports (Madani et al., 2006; Mahmoodi et al., 2007; Stapleton et al., 2007). Immobilization of TiO_2 on pumice stone is an easy an efficient method to obtain photocatalytic oxidation (PCO) without the filtration problem. Examples of applications are given with the degradation of dyes and dye industry pollutants (Rao et al., 2003). Reviews are available in the literature (Pozzo et al., 1997) on the supported titanium photocatalyst as a photocatalyst for water decontamination. A variety of supporting materials, coating methods (Mehrotra et al., 2005) and reactor arrangements have been investigated from engineering as well as from fundamental point of view. But, reports related to degradation of pesticides using these supports are scare. The photodegradation of an insecticide, isoproturon (IP) has been reported using TiO_2 supported on glass rings in a coaxial rector. Studies revealed that after 60 min of phototreatment, IP was completely eliminated and about 80% of dissolved organic carbon (DOC) remained in solution. This efficiency of photodegradation was compared with that using the suspended catalyst in solution and the results indicated that the catalytic activity of TiO_2 is not reduced when it is

immobilized (Parra et al., 2002). Therefore, for the degradation and complete mineralization of non-biodegradable pesticides used widely in localized region, AOP's as pre/post treatment seems to be better alternative than conventional treatment methods.

Giornelli (2004) studied the dip-coating technique using metallic alcoholates for the grafting of TiO_2 on aluminium foil or aluminium plates, which is controlled by X-ray photoelectron spectroscopy (XPS). The dip coating is shown to be a valuable technique to deposit desired amounts of vanadium oxide on titania, and thus to control the species grafted on the support. Photocatalysed mineralisation of methylene blue using TiO_2 coated onto naturally buoyant polystyrene beads was studied by Fabiyi et al. (2000). Titanium dioxide was coated onto polystyrene using a thermal treatment procedure. The coated beads showed high mechanical stability as well as impressive photocatalytic activity. The catalyst activity remained appreciably high for up to 10 successive runs. These works show that rates in the case of fixed catalytic systems increase with increased turbulence.

Rao et al. (2003) had proposed an easy method to immobilize TiO_2 for photocatalytic transformations of organic pollutants in aqueous solution. It consists of impregnation of pumice stone pellets with commercially available TiO_2. Pumice stone is a soft material, but this disadvantage can be eliminated by fixing pellets on a hard surface (cement or polycarbonate) and using a thin-film fixed bed reactor. The initial efficiency is higher than with other supports. It decreases slowly with irradiation time and the decrease becomes significant after several days of use. Such phenomenon of ageing is a general problem also observed with suspended TiO_2. Sol–gel derived TiO_2 films utilizing a quartz batch reactor were studied for photocatalytic activities by Balasubramanian et al. (2004). The quartz batch reactor was characterized for

parameters like mixing, recycle, aeration and UV radiation flux, and the TiO_2 coated substrates were used as the photocatalyst. The activities of the catalyst films were evaluated by measuring the degradation rate of 4-chlorobenzoic acid used as a model organic pollutant. Immobilized TiO_2 powder films on stainless steel containing a mixture of anatase and rutile phases were found to be more effective than films that were substantially composed of anatase phase particles. The activity of glass beads coated with TiO_2 powder was compared to the activity of commercially available TiO_2 catalyst beads. While the activity of the commercially available TiO_2 catalyst beads was higher there was significant attrition of the TiO_2 catalyst film.

In these configurations, the TiO_2 catalyst is either suspended in the liquid or supported on the walls of the reactor. The reactor configurations utilizing slurry suspensions of TiO_2, in general, outperform those using supported photocatalysts but a catalyst recovery system is needed which may increase treatment costs. In contrast, if the catalyst is supported directly on the reactor wall it makes replacement of the catalyst impractical. Therefore, it is desirable to have a supported photocatalyst that can be easily replaced, economical and easy to produce.

Recent studies, therefore, focused on the performance of solar photo catalytic reactors for the degradation of contaminated water containing pesticides. The selection of the suitable supporting material for catalyst impregnation is an area of interest.

2.7 Various Materials for TiO_2 Immobilization

Antifungal activity of TiO_2-film against *A. niger* on wood under UVA (365 nm) irradiation was investigated experimentally. The two different TiO_2 solutions were respectively suspended in deionized water for 30 min of pre-sonication to disperse the particles uniformly. Paulownia (size 25 x 25 mm, 2 mm thick) was used as the test substrate to be coated with the TiO_2 photocatalyst film. Another kind of paulownia

surface that is coated with Alkyd paint was used for investigating the inhibition effect on different substrates (Fenga et al., 2009). The coated films were printed by the dip-coating method. The volume of the TiO_2 coating applied to each wood board was approximately 1.5 mg cm^{-2}.

Optimization of method for preparing TiO_2 films to increase the porosity of the coatings on the glass beads, as well as on stainless steel was done. The activity of TiO_2 films obtained on stainless steel substrates via a conventional alkoxide sol–gel method and via a Degussa P-25 powder enriched (PE) variation of the conventional alkoxide method was compared. Stainless steel coupons were coated with TiO_2 by conventional alkoxide sol gel and the powder enriched (PE) sol gel method. These coated coupons were used as the immobilized TiO_2 catalyst in the quartz batch reactor. The surface was free of macro cracks that expose the substrate surface or significant depths to previous layers (Balasubramanian et al., 2004).

The method adopted for the immobilization involves the preformed TiO_2 and does not require expensive precursors. A reactor was made of Cuddapah stone. It is an inert solid support for the immobilization of TiO_2. The TiO_2 was suspended in minimum amount of water (4 g of TiO_2 in 100 ml of water) and 5ml of acrylic emulsion was added under stirring. After cleaning the stone, the TiO_2+acrylic emulsion mixture was spread with a laboratory spray gun. The coated TiO_2 film was left for air-drying. Coating was repeated twice to get a uniform film without pin holes. TiO_2 photocatalyst in such an immobilized form is economical and efficient process for the treatment of effluents at larger scale that may be adopted for diluted wastewaters containing H-acid (Noorjahan et al., 2003).

Impregnation on pumice stone pellets fixed either on cement or on polycarbonate sheet. On cement, pellets were added before hardening of cement and on

polycarbonate they were pasted using chloroform to dissolve the superficial layer of the polymer. Then, the pellets were impregnated with a sonicated suspension of TiO_2 (6 g/60 mL) dried, washed to eliminate the excess of titania and let to dry again before use. The weight of TiO_2 retained was 50–60 g m^{-2}. Pumice stone is a soft material and its fixing over the pellets on a hard slanting plank surface is with cement or polycarbonate. In another study, TiO_2 was impregnated on pumice stone pellets by simply brushing with TiO_2 milk or impregnating TiO_2 milk with conventional soaking, drying and heat treatment methods (Subramanyam et al., 2003). The reactor was built of seven quartz tubes having the following dimensions: length, 300 mm; inner diameter, 16 mm; and outer diameter, 20 mm. The inner surface of the tubes was partly covered with TiO_2 particles, i.e. the catalyst was fixed only to the bottom part of the horizontally positioned tube. The total area (A_t) covered with catalyst, determined for one tube, amounted to 6030 mm^2 (Malato et al., 2002).

2.8 Photocatalytic Reactors for Degradation of Pollutants

Several different reactor models have been proposed and evaluated for the purpose of removing organic contaminants from water. Different models can be classified into two broad categories—slurry reactors utilizing suspended TiO_2 powders and immobilized TiO_2 catalyst reactors. Most of the studies related to photo degradation have been carried out using the suspension of powder TiO_2 in aqueous solutions. However, the use of aqueous suspension is limited for practical application by filtration problems due to the small size of TiO_2 particles. Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of removing the catalyst.

Hussain and Serpone (1988) studied the photocatalytic degradation of phenol, 4-chlorophenol, 2, 4-dichlorophenol, and 2, 4, 5-trichlorophenol over TiO_2 (anatase) by

using three photochemical reactors. The degradation of the four phenolic compounds, in a continuous recirculation mode in all three reactors, approximates first-order kinetics to near-complete degradation. Mozia et al. (2007) investigated the photocatalytic oxidation of Azo dye Acid Red 18 in water in the quartz labyrinth flow reactor with immobilized catalyst bed. The rate constants calculated for dye concentrations of 10 and 30 mg dm^{-3} amounted to 0.228 and 0.176 h^{-1}, respectively. After a total fading of the dye solution, 98% of TOC disappeared when the 10 mg dm^{-3} solution was applied and 99% when 30 mg dm^{-3} was used. Álvarez et al. (2011) performed a comparative study with a pilot scale plant to compare the effectiveness and energy consumption of some advanced treatment methods applied for municipal wastewater reclamation. The studied processes were: adsorption onto activated carbon, ozonation, O_3/H_2O_2, catalytic ozonation (using activated carbon as catalyst), UV-C photolysis and TiO_2 photocatalysis. Pharmaceutical compounds were satisfactorily removed (< 90% removal) with all the treatment methods used but adsorption onto activated carbon (81.4%) and direct photolysis (22%). COD removals were in the range 20.4- 83.3% while satisfactory disinfection (total coliforms in the effluent below 100 CFU/100 ml) was only obtained by ozone and photocatalysis technologies.

Feitz et al. (2000) evaluated two solar pilot scale fixed bed photocatalytic reactors 1.coated mesh reactor and 2.Packed bed reactor for the removal of phenols. By coated mesh reactor the total removal of phenol, for an exposure of 200 min is 36% whereas packed bed reactor achieves 98% removal of phenol from a 2.3 mgL^{-1} of 100 L solution.

Raquel et al. (1996) studied a fixed bed solar reactor using TiO_2 as a photocatalyst in the photodegradation of chlorinated organic compound. TiO_2 was used in the immobilized form using a flat glass plate as a support. The influence of

parameters such as the slope of the plate, solar light intensity, flow rate and molar flow rate, as well as the geometry of the reactor, was studied using dichloroacetic acid (DCA) as a model compound. The photodegradation was favoured at 22^{o} slope, where 95.8% was degraded, while 89% was degraded at a slope of 25^{o}.

Wang et al. (1999) fabricated a jacketed cylindrical type reactor with suspended titanium dioxide under UV-light of 365 nm for decomposition of mono-substituted phenols. The factors studied were the effects of pH, anion additives and the influence of co-existing reactants competing for reaction. From experimental results, under the condition of 7.5 gL^{-1} TiO_2, pH 3, and light intensity of 2.25 mW cm^{-2}, 0.1 mM of substituted phenol could be completely decomposed in 2 h.

Zayani et al. (2009) investigated for the removal of commercial azo dye using solar photocatalytic pilot plant. Experiments were carried out to optimize various parameters, influencing the performance of the operated thin-film fixed bed reactor (TFFBR) with an area of $25m^2$. The results showed kinetic dependency on flow rate, catalyst loading, and initial dye concentration.

Tennakone et al. (1995) studied photocatalytic degradation of organic contaminants in water with TiO_2 supported on polythene films. The insignificant quantity of carbon dioxide detected from degradation of phenol by UV light, which could be impurities present in polythene. It was seen that more than 50% phenol has got degraded in 2.5 h. Chin et al. (2004) successfully studied synthesization and immobilization of TiO_2 thin film photocatalyst on glass reactor tube using sol-gel method. In the tubular photocatalytic reactor, 5 re-circulation passes with residence time of 2.2 min (single pass) degraded 50% of 40-lM methylene blue dye.

Chan et al. (2003) constructed a solar photocatalytic cascade reactor to study the photocatalytic oxidation of benzoic acid in water under different experimental and

weather conditions. Nine stainless steel plates coated with TiO_2 catalyst were arranged in a cascade configuration in the reactor. A turbulent flow pattern and, hence, improved mixing in the liquid film were achieved due to unique cascade design of the reactor. The percentage removal of TOC of 100 mg L^{-1} benzoic acid solutions increased from 30% to 83% by adding 10 mL of hydrogen peroxide solution (30wt%). Hydrogen peroxide was also shown to enhance the efficiency of the degradation process at elevated temperatures.

Macounová et al. (2001) studied the photodegradation of metamitron in aqueous solution (i) on a plate photoreactor with immobilized TiO_2 layer and (ii) in a tube photoreactor in the presence of quantum sized Q-TiO_2 particles. Both processes, heterogeneous photocatalysis and homogeneous direct photolysis, took part on the overall photodegradation of metamitron. Deaminometamitron hydroxymetamitron and deaminohydroxymetamitron were identified as main products.

Kamble et al. (2006) studied photocatalytic degradation of phenoxyacetic acid (PAA) in batch as well as in continuous photoreactor using concentrated solar radiation. A comparison of photocatalytic degradation of PAA with 2, 4-Dichlorophenol showed that phenoxyacetic acid degrades more rapidly than 2,4-Dichlorophenol under the otherwise identical conditions. It has been shown that PAA can be degraded using concentrated solar radiation/air/TiO_2 system in a continuous bubble column reactor. Noorjahan et al. (2003) studied photocatalytic degradation of H-acid over a novel TiO_2 thin film fixed bed reactor and in aqueous suspensions. The study included dark adsorption experiments in different pH conditions, influence of the amount of photocatalyst, effect of H-acid concentration, effect of pH on chemical oxygen demand (COD), biological oxygen demand (BOD) and the sulphate ion

formation during the photocatalytic degradation. Photocatalytic treatment significantly reduced COD by 62% and increases BOD at the end of third day.

Granular activated carbon (GAC) fixed bed adsorption; the continuous photocatalysis systems and a combination of the two were studied by Areerachakul et al. (2007) to evaluate their capabilities in removing the herbicide of metsulfuron-methyl (MM) from waste water. Removal of MM via adsorption using GAC fixed beds of 5, 10 and 15 cm depths achieved a removal of 35, 55 and 65% of MM respectively. In the continuous photocatalysis system, heterogeneous photocatalysis with TiO_2 was used to degrade MM. The system achieved removal rates between 40 and 60%. Chiou and Shei (2006) demonstrated decomposition of 5mg L^{-1} di-n-butyl phthalate (DBP) upto 75% in 80 min. reaction time in a photo-reactor containing glass beads coated with titania.

Miranda and Suarez (2011) observed 85% degradation of low concentration emerging contaminants in the municipal wastewater (acetaminophen, antipyrine, atrazine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan) in 120 minutes in a pilot compound parabolic collector (CPC) plant which employed glass spheres dip coated with titania. In another study, Rao and Chaturvedi (2012) investigated the decoloration and mineralization of textile wastewater using pebble coated with catalyst in the direct sunlight.

2.9 Solar collectors for water treatment

Traditionally, solar collector systems have been classified in two broad groups depending on the degree of concentration reached in them (i) non-concentrating that are static and have no solar tracking like flat plate reactor (Luna et al., 2010), compound parabolic collectors **(**Blanco and Malato, 1999) and (ii) high-concentrating that are

controlled by a solar tracking system on one or two axes that keeps the collector aperture plane always perpendicular to the solar rays. In this situation, all solar radiation available on the aperture plane is reflected and concentrated on the absorber tube that is located in the geometric focus of the parabola (Arasu and Somakumar, 2007; Mcloughlin et al., 2004; Bahnemann, 2004; Matthews, 1986; Nogueria and Jardim, 1996). In terms of wastewater treatment designs, reactors based on non-concentrating category are more mature having flexible working conditions, controlled concentration ratio (ratio of collector aperture area to the absorber area) and temperature. Designs of non-concentrating solar reactors (one sun) include tubular (Malato et al.,2004), double-skin (Nogueria et al., 1996), shallow pond (Wyness P et al.,1994), falling film (Nogueria et al., 1996), coated mesh (Feitz et al., 2000), cascade (Xi et al., 2001; Chan et al., 2003; Guillard et al., 2003) and fountain (Puma et al., 2001).

Compound parabolic collector (CPC) is the widely applied and best tested design with excellent efficiency in non-concentrating solar reactors. The efficiency is the measurement of the performance of a collector, defined as the ratio of energy achieved to incident solar energy for the same period of time (Duffie and Beckman, 2006). The possibility of integrating photocatalysis and solar technologies (Clark et al., 1978; Jannot 1997; Hegazy et al., 1999) has triggered further attention because of lower treatment costs due to the use of renewable solar energy.

2.10 Scale-up photocatalytic degradation studies

Recent literature has established the potential of AOP as a powerful technology to destroy toxic pollutants dissolved or dispersed in water. However, viability of pilot plant photo-reactor is very important for making this technology commercial reality (Alexiadis and Mazzarino, 2005; Fares et al., 2007). Mukherjee and Ray (1999)

discussed the challenges that need to be addressed for the scale-up of multiphase photocatalytic reactors. Uniform light distribution inside the reactor through the absorbing and scattering liquid to the catalyst, and providing high surface areas for catalyst coating per unit of reactor volume are the two important parameters must be addressed for a new reactor design. Two new design configurations for efficient photocatalytic reactors have been discussed that not only address the solution to both of the above problems but also have scale-up potential.

Puma et al. (2007) studied the feasibility of scale-up studies of photocatalytic oxidation of the herbicides isoproturon, simazine and propazine over irradiated TiO_2 (Degussa P25) from laboratory data to plant-scale. The reactor used for the photocatalytic oxidation was laboratory-scale annular photo-reactor operated in recirculation batch mode. The multi-component kinetic model established was then extended to take into account the direct effect of radiation absorbed by the TiO_2 photocatalyst in order to obtain intrinsic kinetic parameters independent of the radiation field in the photo-reactor. The resulting rate kinetics from lab data was then used to predict, through accurate reactor modelling, the degradation of the herbicides in an optimal configuration of a flow-through, pilot-scale, falling film photoreactor.

Sarria et al. (2003) presented an innovative coupled solar-biological system at field pilot scale for the degradation of a model biorecalcitrant compound, 5-amino-6-methyl-2-benzimidazolone (AMBI). As the photo-Fenton system was fast and effective method, it was selected as most appropriate AOP for the degradation of a model biorecalcitrant compound. For optimizing the concentrations of Fe^{3+} and H_2O_2, the Response Surface Methodology was used. The strategy to develop this system implicates the choice of the most appropriate solar collector and the most efficient AOP, the optimization of this AOP, the choice of the biological oxidation system. The

coupled system was operated in semi-continuous mode, had demonstrated the whole mineralization performance between 80 and 90% in the range of initial dissolved organic carbon (DOC) concentration of 300–500 mg Cl^{-1}. These results indicated that coupling solar-biological processes at pilot scale was a plausible effective approach for the treatment of real industrial wastewaters.

The possibility of coupling AOP (pre or post treatment) with conventional biological systems for the treatment of pesticides has been well documented in literature. Zapata et al. (2010) have proposed design strategy for an industrial combined solar photo-Fenton/aerobic biological system for the decontamination of wastewater polluted with commercial pesticides. Both the possibilities (photo-Fenton/bio and Bio/photo-Fenton) of the combined system were evaluated in pilot plant and the most successful was scaled-up. Compound parabolic collector was used for photo-Fenton at an initial DOC of 500 mg L^{-1} (100 mg L^{-1} of each commercial pesticide). The biological pilot reactor was an Immobilized Biomass Reactor (IBR) filled with polypropylene Pall Ring supports colonized by activated sludge. The industrial plant has a total collector surface of 150 m^2, total photo reactor volume of 1060 L and the scaled-up biological treatment plant (also an IBR) consists basically of two IBRs (1230 L each).

The photo-Fenton treatment at pilot plant scale was able to reduce toxicity (from 96% to 50% of inhibition) and increase biodegradability (from 50% to 95%) of the wastewater and the most suitable point for combining it with the biological treatment was after the total elimination of the active ingredients. The efficiency of the combined photo-Fenton/bio system in terms of mineralization was 94%, of which 35.5% corresponds to the AOP and 58.5% to the aerobic biological treatment. The combination Bio/photo-Fenton was not successful. The efficiency of the industrial-

scale combined system (photo-Fenton/bio) was 84%, 35% corresponding to the photo-Fenton treatment and 49% to the biological stage.

Wisely designed photocatalytic reactors can decrease energy consumption or can avoid post-separation stages in photocatalytic water treatment processes. Doping nano- crystalline titanium dioxide (NTO) with metals or non-metals can reduce the band gap of the doped catalyst, enabling light absorption in the visible region. Coupling NTO photocatalysis with other water-treatment technologies can be more beneficial, especially in large-scale treatments (Lazar et al., 2012).

A new twin 75-L compound parabolic collector (CPC) pilot plant driven by solar energy was used by Maldonado et al., 2007 for the treatment of several different pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) considered priority substances (PS) by the European Commission dissolved in water. Titanium dioxide photocatalysisand photo-Fenton were applied for the degradation of selected pesticides. Total organic carbon (TOC) mineralisation, disappearance of the parent compound and inorganic ion release are discussed as a function of treatment time. Photo-Fenton treatment was found to be shorter than TiO_2 and more appropriate for these compounds and mixtures of them.

2.11 Summary

Photocatalytic technologies (AOP) have proved their potential for the treatment of biorecalcitrant compounds like dyes, phenols, chloro-phenols, pesticides etc. present in water/wastewater. These compounds being toxic show resistance to biological and chemical treatment. AOP are successful in degrading and mineralizing these bio-recalcitrant compounds and proves to be the only effective treatment.

TiO_2 photocatalysis, in slurry form, is an important approach of AOP to degrade toxic compounds as it is chemically inert, stable, strong oxidizing power and

relatively inexpensive. Although successful in many applications, titanium dioxide uses small portion of solar spectrum. Catalyst separation from the slurry always poses a problem, thus hindering its practical applications. The photocatalytic treatment and degradation has been reported using fixed/immobilized catalyst on various inert supports like wood, clay, pumice stone, glass beads, ceramic beads, stainless steel and other metals. Success of fixed-catalysis at lab and pilot-scale has shown their potential for commercial applications but, mass transfer limitations remain their core problem. The durability, cost and recyclability of the immobilized system have not been effectively addressed. Moreover, the inertness of support material is also a major concern, which has not been stressed upon.

In recent literature, many design developments have been discussed in the field of solar reactors. The studies have shown the effectiveness of concentrating type reactors in degrading wide variety of compounds but their higher capital cost always raises the economics of the AOP. Whereas, non-concentrating solar reactors are more economical to use and they have potential for treating large amount of wastewater containing toxic compounds. Only few studies have been reported on the commercial demonstration of non-concentrating slurry reactors using solar radiations. Hence, more studies are required in the field of slurry reactors for their design modifications, operating conditions with process optimization.

2.12 Objectives of the work

Last one decade has marked good footprints in the area of wastewater treatment using Advanced Oxidation Processes (AOP). The areas of application ranges from different industries textile, pulp and paper, pesticides etc to municipal water. Plenty of research has been done on synthetic compounds used in industries and agriculture practices since last few years but considerable gap has been noted on their applications in terms of time and cost effectiveness. Still cost of operating AOP's is a major concern for all the research units due to high electrical energy requirements. For its industrial applicability, photocatalysis using natural solar radiations is the need of the hour, so research is required in this direction to make the process cost and energy effective.

Therefore, the work was undertaken to study the photocatalytic degradation of two commonly used pesticides in the region using lab-scale slurry pond reactor and fixed-bed reactor along with pilot-scale studies with both slurry and fixed reactors. Process optimization was done and kinetic studies were done.

The objectives proposed were:

- To study the photocatalytic degradation of pesticides commonly used in agricultural practices in the state of Punjab, using titanium dioxide (TiO_2-Degussa P25) and to investigate the effects of the operating variables on the process
- To attempt scale-up trials with the optimized parameters as solar pond type reactor for effective degradation of the pesticides under study

Chapter 3

MATERIALS AND METHODS

This chapter deals with materials used and various methods adopted for carrying out the study in context to the degradation of pesticides.

3.1 Pesticide sample collection

Technical grade pesticides (Isoproturon and Imidacloprid) with purity 99% used for the study were received as gift samples from Pioneer Pesticides Private Limited, Chandigarh (India) in sealed bottles with all the safety precautions data. Pesticides were stored at 4 ^{o}C before they could be used further. For experimental studies, stock solution of pesticide of 25 mg L^{-1} was prepared and used further in photocatalytic studies except for initial concentration experiments.

3.2 Isoproturon

Technical grade of Isoproturon (IPU), N,N-dimethyl-N′-[4-(1-methylethyl)phenyl] urea, (95%), structure of which is shown in Fig. 3.1, was obtained from Pioneer Pesticides Pvt. Ltd, Chandigarh (India) and used as such without any further purification.

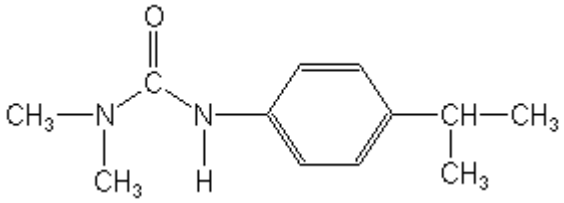


Figure 3.1: Chemical structure of Isoproturon

IPU is mainly used for control of annual meadowgrass, blackgrass, ryegrass, silky bentgrass, wild oat, and many broadleaf weeds. This herbicide enters the

environment during its application in agricultural fields, but may also occur during manufacture, transportation and storage (WHO).

3.3 Imidacloprid

Imidacloprid[1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidenamine] a relatively stable chloronicotinic insecticide, classified as Category I due to its high leaching potential (USEPA, 1993). It could easily contaminate water sources, leading to negative environmental and health effects. Indeed, acute exposure to Imidacloprid may cause apathy, spasms and thyroid lesions (fig. 3.2).

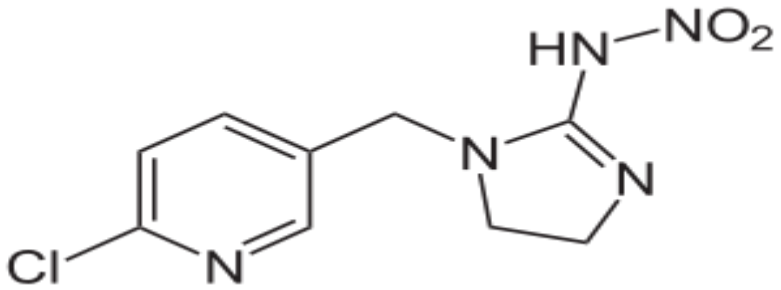


Figure 3.2: Chemical structure of Imidacloprid

It is known to affect mammalian reproduction. In insects, Imidacloprid acts as an agonist on the postsynaptic nicotinic acetylcholine receptors of motor neurons. This causes an overstimulation of the nervous system, and ultimately death.

3.4 Titanium dioxide P-25

The photo catalyst used was titanium dioxide (TiO_2) P-25, a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30, with a BET surface area of 50 $m^2\ g^{-1}$ and average particle size of 30 nm procured from Evonik Industries Pvt. Ltd, India.

3.5 Reagents and chemicals

Hydrogen peroxide, H_2O_2 (30% v/w, AR grade) was supplied by Ranbaxy, India. For COD estimating, COD reagent (containing silver sulphate and concentrated sulphuric acid (SD Fine Chemicals Ltd. India) and ferroin indicator were used. For

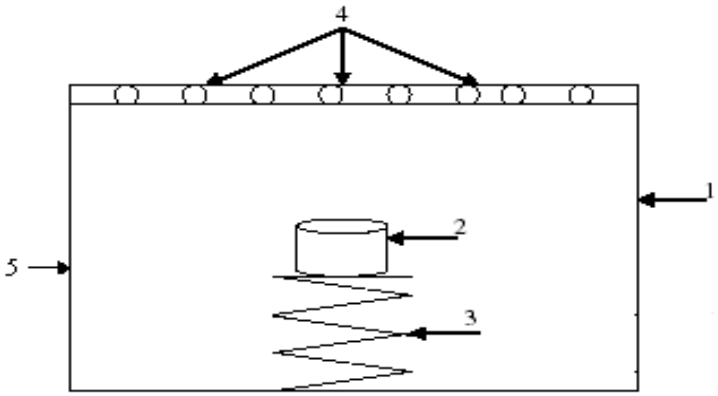
determination of BOD, phosphate buffer, calcium chloride, ferric chloride, magnesium sulfate, manganese sulphate, potassium iodide, sulphuric acid, sodium thiosulphate and starch were used. All other reagents were of analytical grade (SD Fine Chemicals Ltd. India) and were used as received without any purification. In all the experiments, doubly distilled water was used for preparation of stock solution.

3.6 Slurry and fixed bed reactors

3.6.1 Lab-scale slurry photo reactor set-up

The photocatalytic experiments with TiO_2 in slurry form were done in lab scale batch reactor made up of borosil glass, 16 cm in diameter and 5.2 cm in height with a capacity of 1200 mL (Fig. 3.3 a & b). The glass reactor was covered with transparent thin sheet of plastic to prevent evaporation losses simultaneously allowing maximum penetration of UV light. This glass reactor was placed on lab jack in UV chamber (wooden) having dimensions of 4.5 ft x 3.0 ft x 3.5 ft, with 36 W UV tubes (Philip's India) attached on the underside of the roof having wavelength of 365 nm (Toor et al., 2007). During photocatalytic degradation studies, UV intensity was measured using Eppley radiometer (model no. 33013, TUVR, USA).

(a) 



(b)

Figure 3.3: Actual (a) and Schematic (b) diagram of lab scale set up: (1) UV chamber (2) Reactor (3) Lab jack (4) UV lamps (5) Exhaust fan

3.6.2 TiO_2 Immobilization

Beads with average diameter ranging from 1.0 cm to 2.5 cm were prepared from the mixture of cement and sand. TiO_2 was coated on cement beads by dispersing the beads in the TiO_2 slurry until uniform deposition was achieved. To evaporate the excess water, the beads were exposed to 110 ^oC in lab oven. For the total deposition of the catalyst, beads were further calcined at 400 ^oC in muffle furnace for 2 h. The same cycle was repeated for two times for getting uniform and stable layer of the catalyst (Fig. 3.4).

The coated beads were washed with water after each cycle to remove the loosely bound catalyst particles. The morphology of freshly coated TiO_2 bead and recycled bead was studied using SEM (JSM-6510LV, JEOL, Japan) and EDS (INCAX-act, Oxford instruments, United Kingdom) for confirming the stability of TiO_2 layer. Thickness of TiO_2 on the cement bead is approx. 35μm as cleared from SEM image (Fig. 3.5).

Figure 3.4: TiO_2 coated cement beads used for the degradation studies

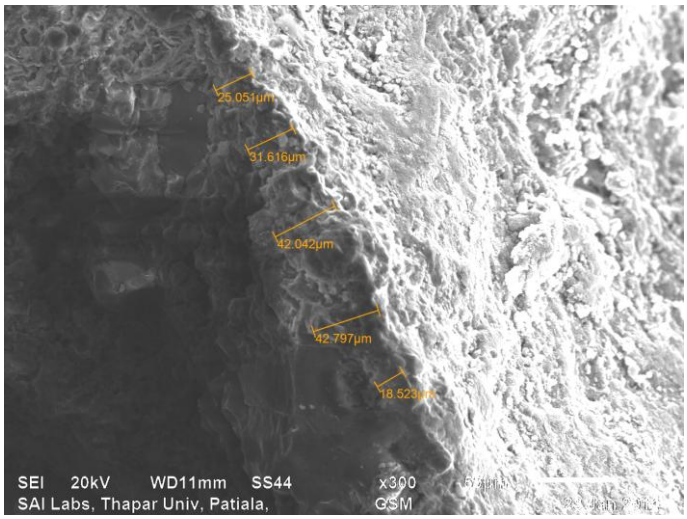


Figure 3.5: SEM image showing average thickness of TiO_2 on cement beads

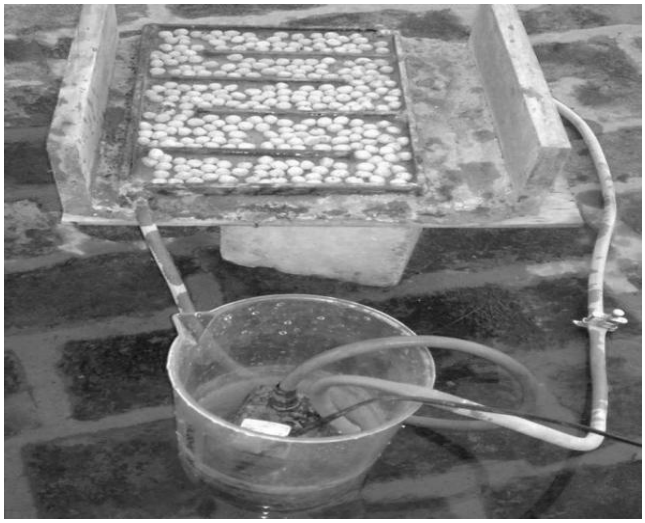


Figure 3.6(a): Actual set-up of solar fixed-bed baffled reactor (SFBBR)

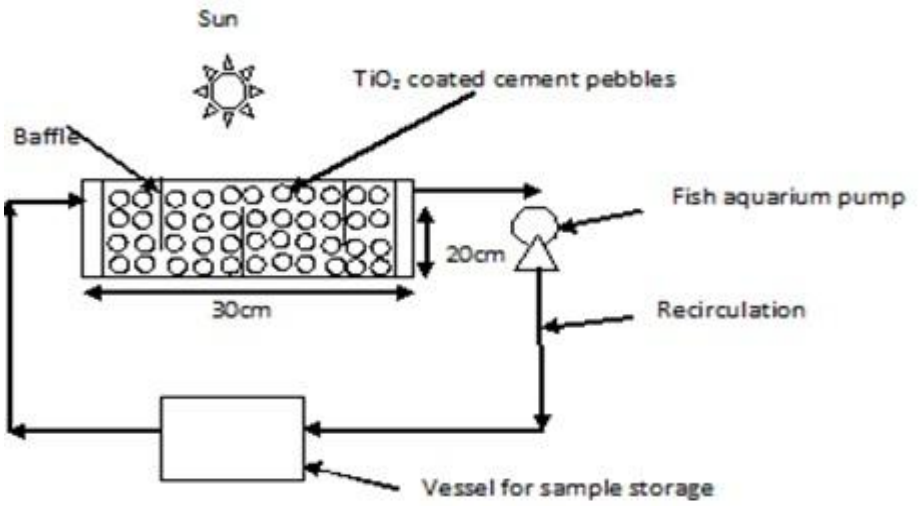
3.6.3 Lab-scale photo reactor set-up using coated beads

The photocatalytic experiments with TiO_2 coated cement beads were done in lab scale batch reactor as well as pilot scale reactor. The batch reactor was made up of borosil glass, 16 cm in diameter and 5.2 cm in height with a capacity of 1200 mL. This glass reactor was placed on lab jack in UV chamber (wooden) having dimensions of 4.5 ft x 3.0 ft x 3.5 ft, which had 36 W UV tubes (Philips) attached on the underside of the roof having wavelength of 365 nm for getting required intensity in the chamber (Toor et al., 2007). For the batch photocatalytic experiments, 300 ml solution containing the appropriate amount of immobilized catalyst beads was irradiated for 3-4 h under UV irradiations. At regular intervals, an aliquot of 3 mL was taken from the reaction volume. The sample was filtered using Millipore filter (0.45 μm). The UV intensity was varied by adjusting the height of lab jack from 10 to 28 W m^{-2} corresponding to the average intensity of UV radiation available in sunlight. Aeration was done by purging oxygen at required flow rate from time to time. For proper control of temperature inside the chamber, an exhaust was provided. All experiments were carried out in triplicate for reproducibility of results.

3.6.4 Pilot-scale fixed-bed photo reactor

3.6.4.1 Fixed-bed baffled solar reactor

The pilot scale set-up consisted of a baffled reactor 30 cm x 15 cm made up of concrete with four baffles at equal distances (Fig. 3.6 a). The TiO_2 coated cement beads were placed in each chamber of baffled reactor in such a way that they are effectively submerged in the solution to be treated the top view of which is shown in Fig. 3.6 b. The flow rate of the pesticide solution was maintained for getting the required retention time. The reactor was covered with transparent sheet for easy penetration of sunlight besides controlling evaporation losses.



(b)

Figure 3.6 (b): Line diagram of solar fixed-bed baffled reactor (SFBBR)

3.6.4.2 Fixed-bed parabolic trough collector

A solar parabolic concentrator (Ecosense Sustainable Solutions Private Limited, New Delhi, India) which reflects the solar radiation onto a glass receiver tube was used in this study with specifications given in table 3.1. The solar receiver was made of a transparent borosil glass with rubber cork at both ends of the glass tube. An automatic tracking system was installed in the collector to concentrate maximum solar radiation at the focal tube (Fig. 3.7). The receiver tube was packed with sufficient number of coated TiO_2 cement beads. The solution with known concentrations of pesticide and oxidant was pumped from the storage tank through the receiver tube at the flow rate of 1 L min^{-1}. Temperature of the circulating solution was recorded by temperature sensors. UV intensity was also measured by radiometer. Samples were taken at regular intervals of 30 min and analyzed for degradation.

Table 3.1: Specifications of parabolic trough collector (PTC)

Items	**Value**
Rim angle	90^0
Focal distance	0.2 m
Collector aperture	0.8 m
Receiver diameter	12.8 mm
Collector length	1.25 m
Concentration ratio	19.89
Water flow rate	0.5-2 $Lmin^{-1}$
Storage tank capacity	7 L
Tank material	Stainless steel
Water pump	367.65 W

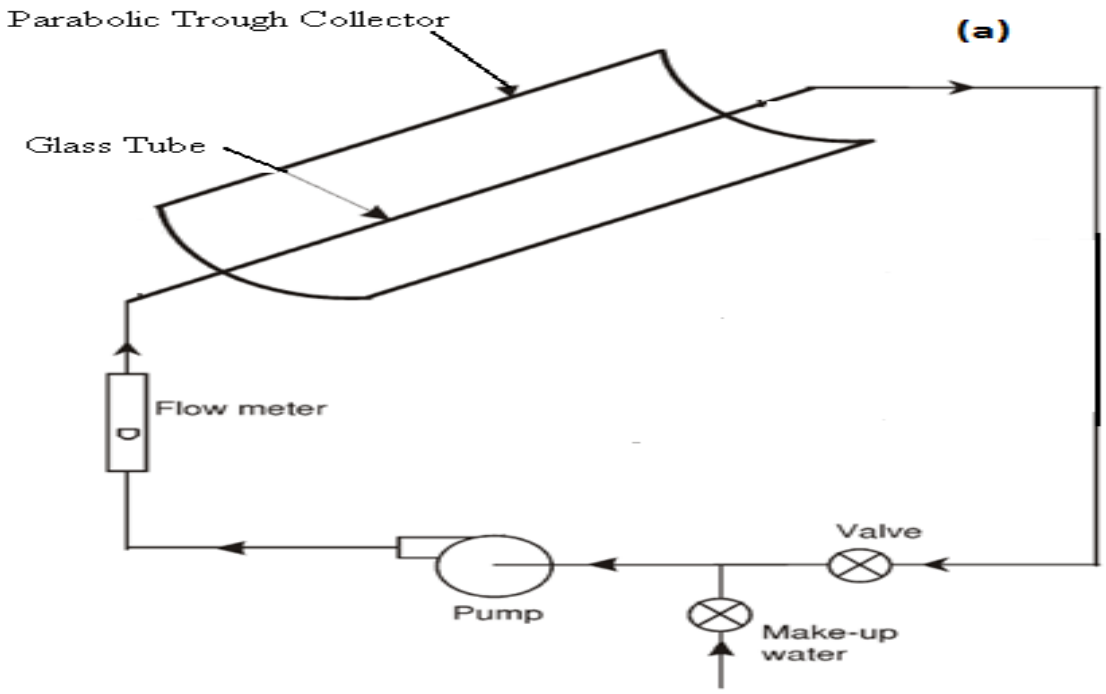


Figure 3.7: (a) Schematic diagram of parabolic trough collector (b) Actual site photograph of Parabolic Trough collector.

3.7 Experimental procedures for heterogeneous and homogeneous photocatalytic studies

3.7.1 Shallow pond slurry reactor

Stock solution of pesticide was prepared in double distilled water for all the experiments. The UV-tubes were turned on and allowed to warm-up for 30 minutes before the experiment was started. 200 ml of pesticide sample with initial concentration of 25 mg L^{-1} was taken in the batch reactor and the optimum amount of catalyst was added. Initially solution was kept in dark for 30 min for allowing adsorption equilibrium. This solution was then kept under UV-lamp in the chamber with continuous stirring using magnetic stirrer for the required period. An aliquot of 3 ml was taken from the reactor at the regular intervals of time with the help of syringe. The catalyst was filtered out from the sample by Millipore filter (0.45 μm). These samples

were analyzed using UV-spectrophotometer as well as by COD estimation. For pH adjustments, digital pH meter (CP 901, Century, India) was used. The pH of solution was adjusted with the help of buffer solutions.

All the experiments were carried out under the normal reaction conditions at intensity of 20 -28 Wm^{-2} and carried out twice to check the reproducibility of results. The percentage error in all the experiments was in the range of 1-5%.

3.8 Analytical analysis

3.8.1 UV -Vis spectrophotometer analysis

The treated samples were analyzed using UV -Vis spectrophotometer (HITACHI U-2800, Japan). The samples were filtered through Millipore filters (0.45 μm) and absorbance of the compound was measured at corresponding λ_{max} (Isoproturon at 239 nm and Imidiacloprid at 269 nm). From standard solutions, calibration curves were prepared and concentrations of experimental solutions were thus determined.

3.8.2 Estimation of COD

COD was determined as per the American Public Health Association (APHA) standard method (APHA, 1992: Sec. 5220C). A sample was refluxed in strongly acid solution (COD reagent) with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ was titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter was calculated in terms of oxygen equivalent. For blank studies, distilled water was taken in place of sample and rest of the steps are same.

$$\text{COD (mg } O_2 \text{ / liter)} = [(A-B) \times M \times 8000] / \text{ml sample}$$

Where, A = Blank reading for ml of FAS used

B = ml FAS used for sample reading

M = molarity of FAS

3.8.3 HPLC analysis

The samples were also analysed using high performance liquid chromatography (HPLC) [Shimazdu, SED-20A, Japan] for the confirmation of isoproturon degradation. HPLC was performed on isocratic HPLC system with C-18 column (250 mm x 4.60 mm), particle size- 5 micron using water:acetonitirile (60:40) as mobile system with UV detector at 239 nm for isoproturon. Flow rate was maintained at 0.5 mL min^{-1}.

3.8.4 LC-MS and GC-MS analysis

The degradation products for isoproturon were analyzed by Agilent series LC-MS equipped with an ESI source. The column used was Exclipse XDB C-18 (1.8 um, 4.6 x 150 mm) and the mass spectrum was operated in positive ion mode. The operating conditions are: gas: helium; gas temperature: 350 ^{o}C with flow rate 10 L min^{-1}; nebuliser gas and nitrogen gas pressure: 450 psi; sheath gas temperature: 320 ^{o}C; sheath gas flow rate: 10 L min^{-1}; capillary voltage: 3500 V (positive); nozzle voltage: 0 V and ionization: positive.

GC-MS was used for determining the degradation products of imidacloprid. The column was TR 5MS (60m x 0.25mm x 0.25 µm). The operating conditions are: carrier gas: helium; Injector: Split mode; transfer temperature: 290 ^{o}C with flow rate 20 L min^{-1}.

3.8.5 Total organic carbon

The total organic carbon (TOC) concentration was determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. In the outside vial, organic carbon in the sample was digested by persulfate and acid to liberate carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent resulting in formation of carbonic acid that changes the pH and thus the colour of the indicator solution. The extent of colour change is related to the

original concentration of carbon in the sample. The measurement wavelengths were 598 and 430 nm for spectrophotometer or 610 nm for colorimeter (Harp 2002).

3.8.6 Estimation of BOD

BOD was estimated as per APHA (APHA, 1992: Sec. 5220C). Samples were diluted to get the BOD in range. The pH of the diluted sample for BOD determination was adjusted between 6.5 and 7.5. Each BOD bottle was filled to just below the lip with seeded or un-seeded dilution solution. Enough dilution water was added to cover the lip of the BOD bottle to make a water seal. After placing a plastic cap over the lip of each BOD bottle and they were dark incubated for five days at 20 °C ± 1 °C. After the five-day incubation period was complete, the dissolved oxygen of each of the samples was determined.

$$BOD = (DO_i - DO_f) \text{ x dilution factor}$$

3.8.7 Estimation of ammonium ions

Ammonium ions (NH^{4+}) were determined using APHA method no. 4500- C (APHA, 1992). 500 mL dechlorinated sample was taken and added 25 mL borate buffer solution and pH was adjusted to 9.5 with 6N NaOH using a pH meter. The sample was distilled at a rate of 6 to 10 mL/min with the tip of the delivery tube below the surface of acid receiving solution. Distillate was collected in a 500-mL erlenmeyer flask containing 50 mL indicating boric acid solution for titrimetric method. Ammonia in distillate was titrated with standard 0.02N H_2SO_4 titrant until indicator turns pale lavender. Carry a blank through all steps of the procedure and apply the necessary correction to the results.

$$\text{mg } NH_3\text{-N / liter} = [(A\text{-}B) \times 280] / \text{ml sample}$$

Where, A = volume of H_2SO_4 titrated for sample, mL, and

B = volume of H_2SO_4 titrated for balnk, mL,

3.8.8 Chlorides estimation

Chlorides (Cl^{-1}) were estimated using APHA method no. 4500-B (APHA, 1992). For chlorides estimation, 25 ml sample was taken in a conical flask. The pH of sample was measured and 1.0 mL Potassium chromate was added as indicator. The sample was titrated with standard silver nitrate solution to pinkish yellow end point and noted down volume of titrant used.

Chloride Ion Concentration (mgL^{-1}) = (A×N ×35.45)*1000 / Volume of the sample

Where: A = volume of titrant used, N is normality of silver nitrate.

Chapter 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter deals with the photocatalytic degradation studies of herbicide isoproturon and insecticide imidacloprid in slurry as well as immobilized form under UV light as well as solar irradiations. Detailed study has been undertaken to study the effect of various operating parameters for both the compounds like catalyst dose, pH and substrate concentration. Variation in intensity of UV irradiations as well as area/volume (A/V) is also studied for the practical applications. Catalyst recycling studies have also been performed to examine the economical viability of the process. Durability studies for the immobilized photocatalyst on the inert support (cement bead) have been carried out. The immobilized photocatalyst system was effectively recycled for at-least twenty to thirty times for degradation of selected compounds. Effect of number of coatings, calcination temperature, size of cement bead etc. has been studied for effective degradation. The identification of intermediate products generated through identification photocatalytic treatment was attempted through LC-MS and GC-MS analysis.

Pilot-scale studies have also been carried out for photocatalytic degradation of compounds. Both slurry and fixed-bed pilot-scale solar reactors have been studied for effective degradation of pesticides under study.

4.2 Photodegradation kinetics studies

For the design and optimization of any industrial system, the understanding of reaction rate is very important. In photocatalytic degradation, the rate depends upon

various parameters like substrate concentration, catalyst dose, pH, oxidant addition, intensity of irradiations. Different kinetic models have been tried for defining the rate of destruction of organics in photocatalytic treatment. Langmuir-Hinshelwood (L-H) kinetics seems to have best fit for most of the photocatalytic reactions. The rate of destruction of organic pollutants according to L-H model is given by:

$$-dC/dt = k_r KC/(1 + K C) \quad (4.1)$$

where, k_r is the reaction rate constant, K is the equilibrium adsorption constant, C the bulk substrate concentration at any time t. For low solute concentration, the factor KC is very small and can be neglected. Photocatalytic degradation rates according to L-H for various organic compounds over TiO_2 can usually be described by a pseudo-first order kinetic expression i.e.

$$-dC/dt = k_r KC = kC, \text{ where, k is apparent rate constant} = k_rK$$

$$\text{or} \quad \ln C_0/C = kt \quad (4.2)$$

C_0 and C are initial and final concentration of the reactant respectively. A plot of $\ln C_0/C$ versus time represents a straight line and slope of which gives k, an apparent first-order reaction rate constant.

4.3 Photocatalytic degradation of herbicide Isoproturon in slurry mode under UV and solar irradiations

4.4.1 Standard calibration curve of IPU

The absorbance of IPU solution was studied between the wavelength of 200 to 800 nm and maximum absorbance (λ_{max}) was obtained at 239 nm. Standard concentrations of IPU were made from 5 mgL^{-1} to 25 mgL^{-1} and their absorbance at 239 nm was measured. An absorbance was plotted against standard concentration of IPU solution to get the calibration curve (figure 4.1). Regression coefficient was found to be

0.9974 and slope was 0.0519. From this calibration curve the unknown concentration of IPU solution can be calculated.

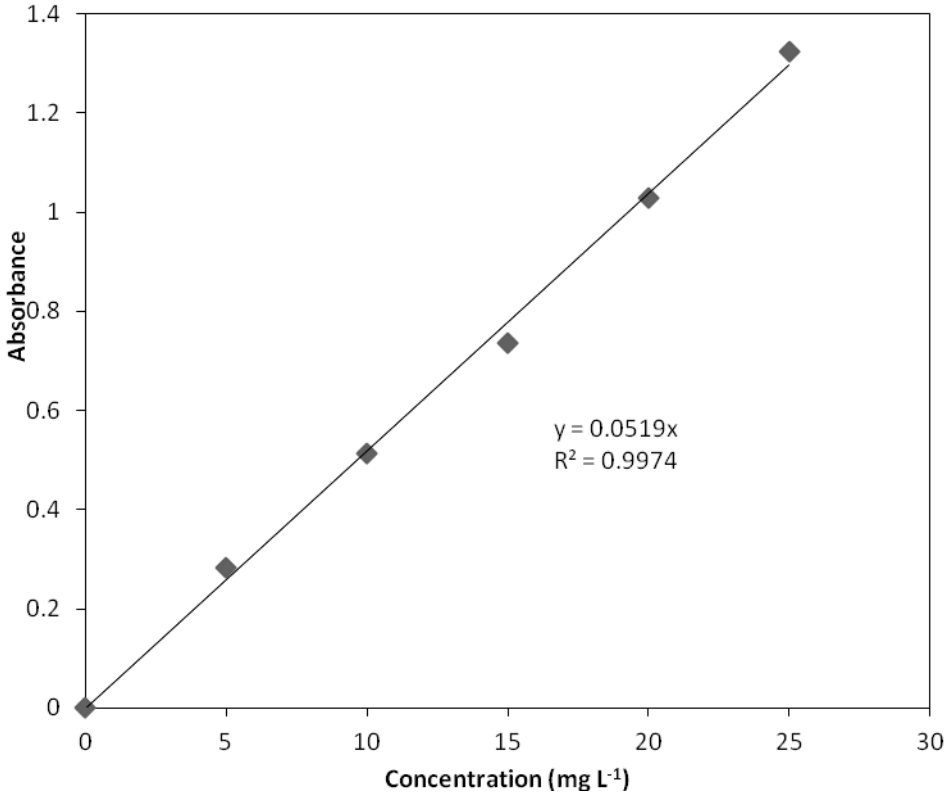


Figure 4.1: Standard calibration curve of IPU

4.3.2 Photolytic and Adsorption Studies

As per the semiconductor photocatalysis, presence of both catalyst and a light source are necessary for the photo-oxidation reaction to occur. In this context, control experiments were conducted on the irradiation of IPU under only UV light without TiO_2 and in the presence of TiO_2 without UV irradiation over a period of 180 min in the batch reactor (Fig. 4.2). The study confirmed negligible photodegradation (6%) of the compound under UV light only, thus indicating that the degradation observed in the presence of catalyst is due to catalyst activity. The reduction of herbicide concentration was negligible (8%) due to adsorption on the surface of the TiO_2 P-25 in dark which is in accordance with Haque and Muneer, 2003.

The reduction in concentration was mainly due to the formation of monolayer of the pesticide on the catalyst surface. No free active sites would be available after the monolayer formation, and therefore no further reduction in concentration was observed. The photocatalytic treatment showed 95% degradation, thus leading to an assumption that adsorption-desorption of the pesticide and reaction intermediates are relatively slow as compared to the formation of electron/hole pairs (Evgenidou et al., 2007).

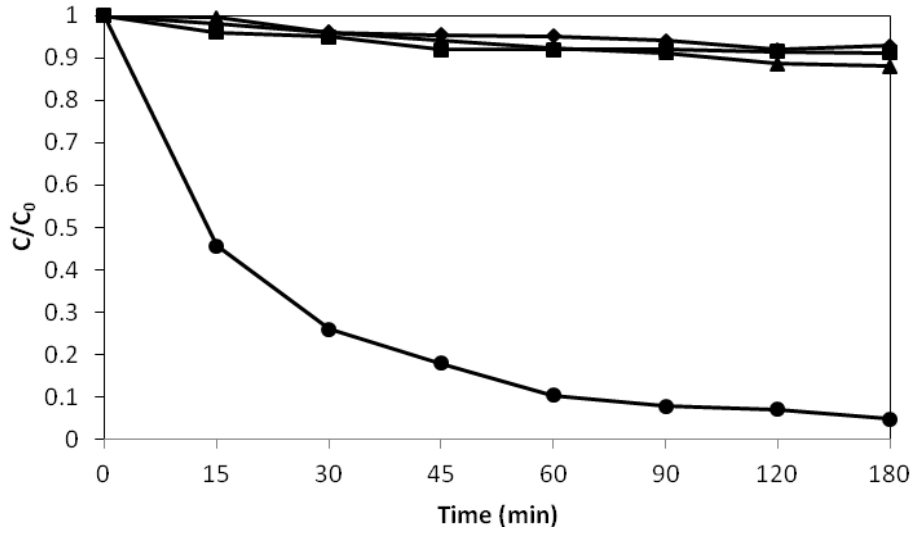


Figure 4.2: Comparison between photolysis and photocatalytic reduction of Isoproturon in the presence and absence of TiO_2 along with adsorption studies (●→UV+TiO_2, ▲→ TiO_2, ■ → UV+ H_2O_2, ♦→ UV). Experimental conditions: 25 mgL^{-1} IPU, V= 200 ml, UV intensity = 23 Wm^{-2}.

4.3.3 Effect of Photocatalyst Concentration

The photocatalyst dose is very important parameter for deciding the efficacy of any heterogeneous photodegradation process. The degradation increases with increase in amount of catalyst but higher amounts after optimum dose are not preferred as it is not economically viable and activity is also reduced. At higher dose of the catalyst, solution becomes turbid resulting lesser penetration of light in solution that leads to reduction of hydroxyl radicals. In our study, TiO_2 concentration was varied from 0.125 to 2.0 g L^{-1} to understand the effect of photocatalyst concentration on the degradation

kinetics of the isoproturon. Fig.4.3 shows a degradation for IPU in slurry batch reactor with different concentrations of TiO_2 and fig. 4.4 shows the plot of the first-order rate constant (k) as a function of the catalyst concentration. It was observed that as catalyst concentration varied from 0.125 to 0.5 g L^{-1}, there was an increase in photocatalytic activity followed by decrease after 0.5 g L^{-1}. Initially, increase in the rate owes to the increase in the number of photons absorbed in UV light with large number of catalyst particles. Aggregation of TiO_2 takes place above a certain concentration of catalyst, causing a decrease in the number of active sites on its free surface leading to reduction in surface area and thus photocatalytic rate. In addition, the higher concentration of the catalyst obstructs the path of light penetrating the solution leading to the scattering of light. All these factors lead to the reduction of $OH^{\bullet}$ owing to decrease in the rate of photocatalytic reaction. A similar kind of effect was studied in the case of photocatalytic degradation of acephate using TiO_2 catalyst using artificial ultraviolet light (Konstantinou and Albanis, 2002; Han et al., 2009). The optimised value is significantly lower than the one reported for degradation of Isoproturon.

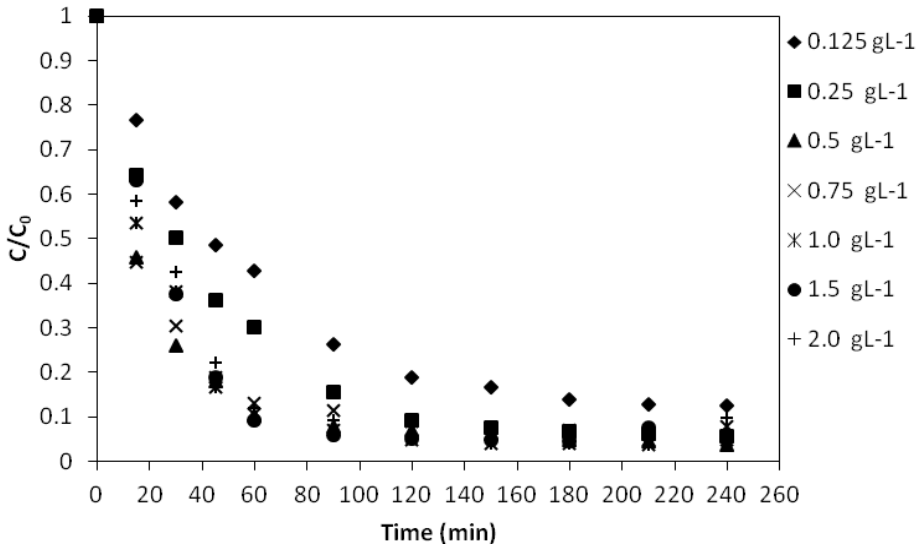


Figure 4.3: Degradation of IPU with varying concentrations of photocatalyst TiO_2 using slurry batch reactor (Volume = 200 ml, pH =6.2, C_0 = 25 mg$L^{-1}$and UV intensity 23 Wm^{-2})

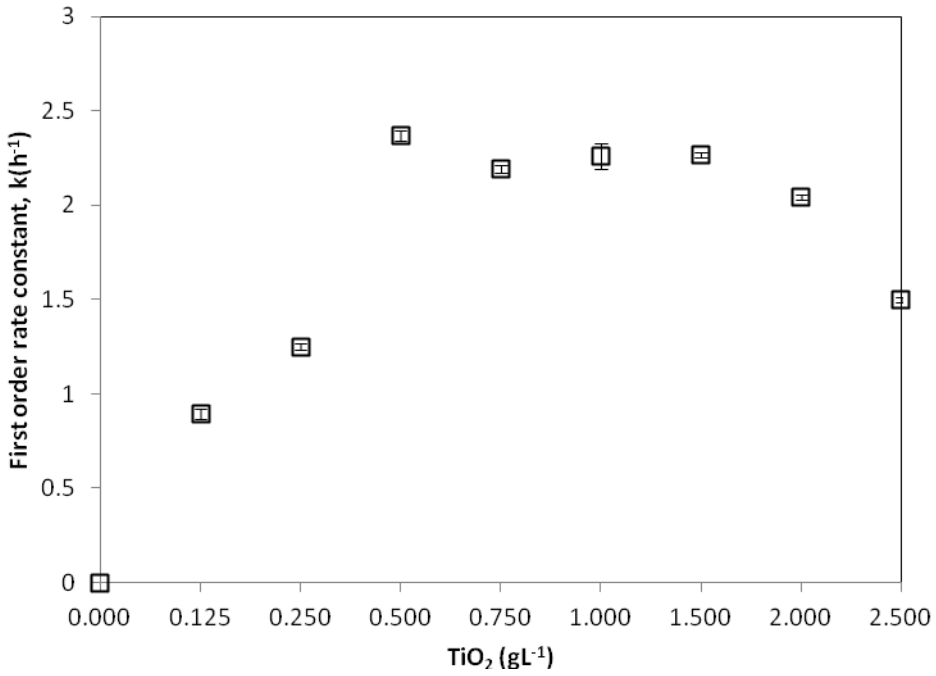


Figure 4.4: Effect of catalyst concentration on the rate constant during photocatalytic degradation of IPU

4.3.4 Effect of Initial Substrate Concentration

The effect of herbicide concentration is an important parameter from an application point of view to study the removal efficiency. In order to study the effect of substrate concentration on the degradation rate, the isoproturon concentration was varied from 5 – 30 mg L^{-1} with optimum catalyst dose of 0.5 gL^{-1} at 6.2 pH (Fig. 4.5).

As the photocatalytic degradation proceeds with the Langmuir-Hinshelwood (L-H) law i.e. the rate is first order at lower substrate concentration and becomes zero order at higher concentrations (Toor et al., 2005). Similar trend has been observed in our studies as degradation rate reached constant after 25 mg L^{-1}. The production of OH radicals by the catalyst is not sufficient in comparison with amount of herbicide adsorbed on the surface of the photocatalyst at higher concentrations. Sufficient data is available in literature suggesting the equilibrium between adsorption of the substrate

molecules on the catalyst surface and the generation of the OH radicals from the active sites (Ollis et al., 1991).

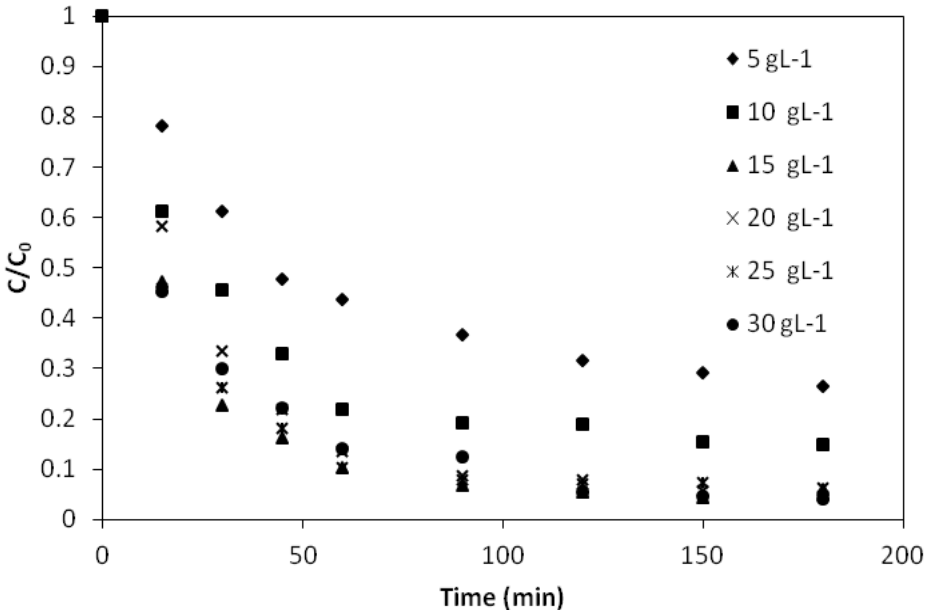


Figure 4.5: Effect of initial concentration on the degradation of IPU at reaction volume = 200ml, TiO_2= 0.5gL^{-1}, pH =5.0, and UV intensity 23 Wm^{-2}

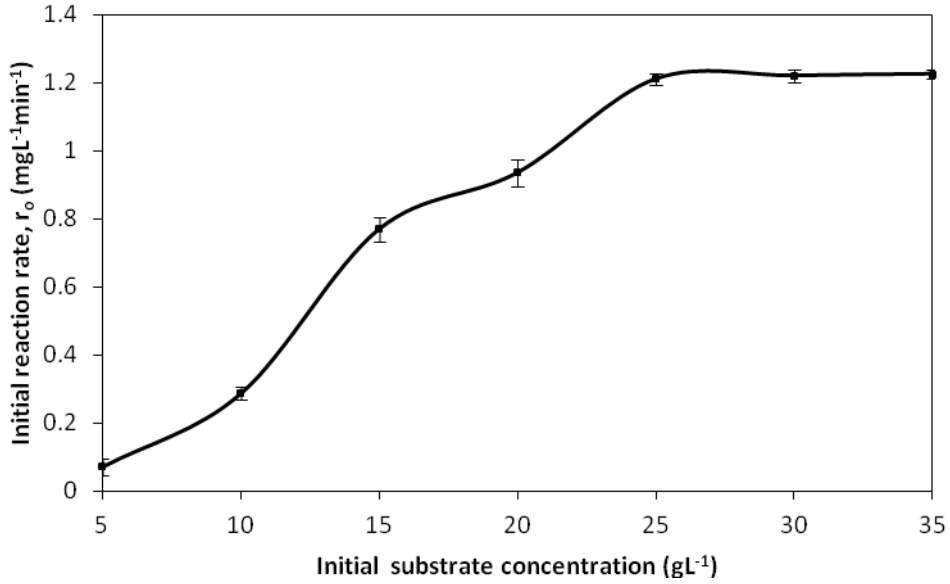


Figure 4.6: Effect of isoproturon concentration on the initial photodegradation rate during photocatalytic degradation

4.3.5 Effect of pH

The pH of the solution plays an important role in photocatalytic reactions taking place on the semiconductor's surface. Initial pH of the solution depicts the surface charge properties of the catalyst and thus the adsorption of the compound. In this context, the effect of initial pH on the photocatalytic degradation of isoproturon is presented in Fig. 4.7 with the optimum amount of catalyst 0.5 g L^{-1} at constant UV intensity of 23 W m^{-2}. In our case, the degradation rate was slightly higher in acidic medium and decreased gradually towards basic medium (Fig. 4.8). In acidic suspensions, the adsorption of an herbicide on the TiO_2 particles increased significantly when compared to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 can develop either a positive or a negative charge on its surface because of its amphoteric nature (Malato et al., 2002). The point of zero charge (pzc) of the used TiO_2 (Degussa P-25) is widely reported at pH ≈ 6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution. Thus, pH value has a significant role in adsorption/desorption properties of the catalyst surface (Hoffman et al., 1995).

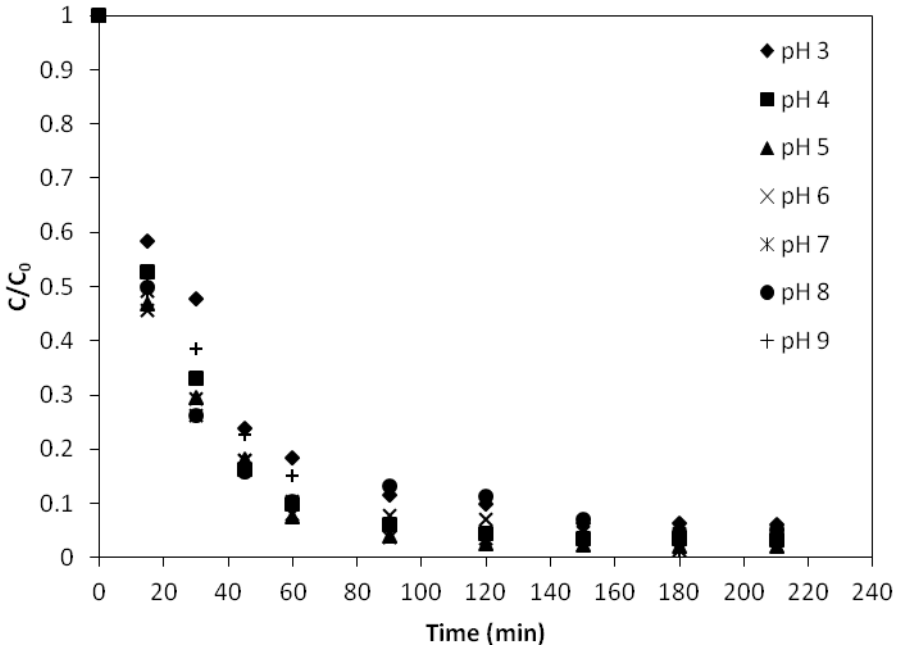


Figure 4.7: Concentration data for the degradation of herbicide IPU at different pH (reaction volume = 200ml, TiO_2= 0.5gL^{-1}, C_0 = 25 mgL^{-1}and UV intensity 23 Wm^{-2})

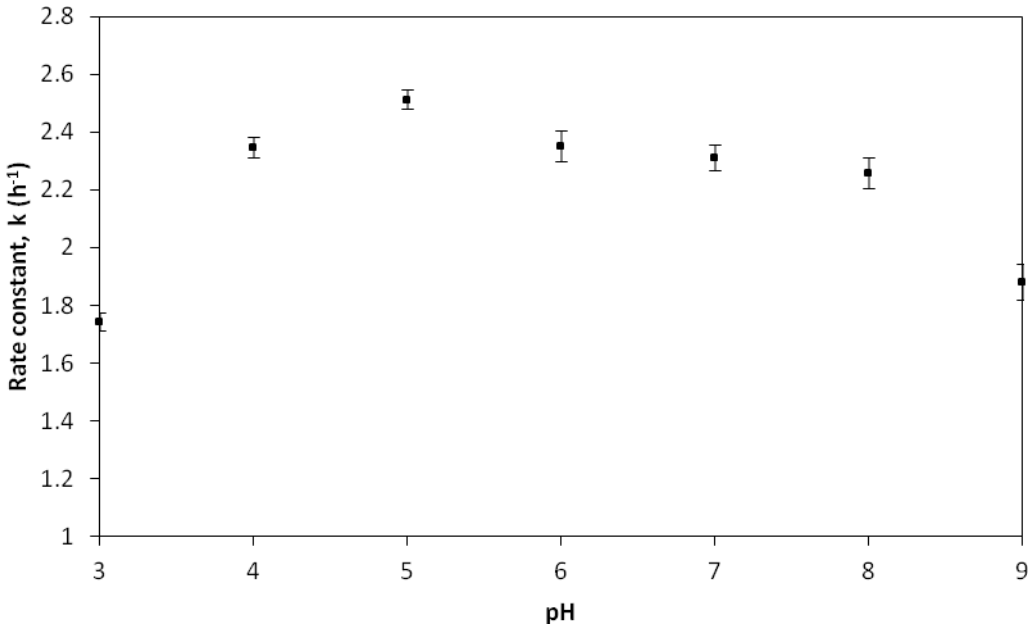


Figure 4.8: Effect of variation in pH on the rate constant during photocatalytic degradation of isoproturon

4.3.6 Effect of UV Intensity

The utilization of sunlight is always preferred for the practical application of AOP in the field. The intensity of solar UV radiations varies throughout the year (Dubey et al., 2009). For shallow pond slurry reactor, the reaction rate constant depends upon intensity as follows:

$$k/k_o = m\,[I(A/V)\,/I_o(A/V)_o]^n \qquad (4.3)$$

where 'm' and 'n' are empirical constants, A is the aperture, V is the volume irradiated and k_o is reference rate constant with reference to reference intensity I_o. Keeping the area/volume (A/V) constant for a particular slurry batch system, the Eq. 4.3 can be rewritten as:

$$k/k_o = m\,[I\,/I_o]^n \qquad (4.4)$$

The equation 4.4 shows that the rate constant k is directly dependent on the intensity of incident radiations, if the A/V is kept constant (Toor et al., 2006). In our study, the aqueous solution of isoproturon with optimum amount of TiO_2 was exposed to different intensity of UV radiations keeping the A/V constant at 1.18 $cm^2\ mL^{-1}$. As the intensity varied from 10 to 23 W m^{-2}, the degradation rate constant increased from 1.026 to 2.478 h^{-1} respectively as shown in figure 4.9. With the increase in UV intensity, more number of OH radicals are produced as more radiations fall on the catalyst leading to high rate of degradation. The value of n and m thus calculated from a plot between reaction rate constant (k) and intensity of incident light, for a constant A/V ratio and found to be 0.9472 and 1.032 respectively (Fig. 4.10).

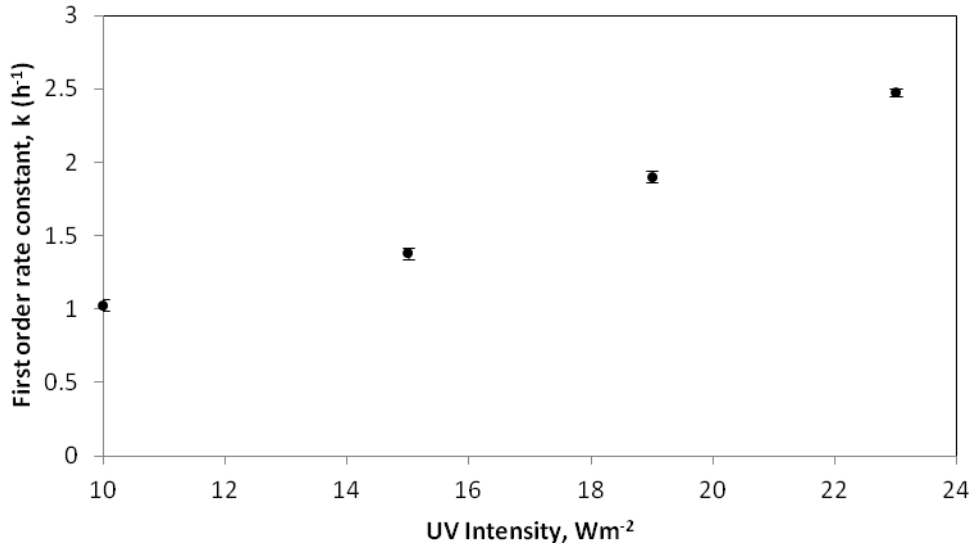


Figure 4.9: Rate constant variation with UV intensity during photocatalytic degradation of IPU (reaction volume = 200ml, TiO_2= 0.5gL^{-1}, C_0 = 25 mgL^{-1}, pH = 5.0)

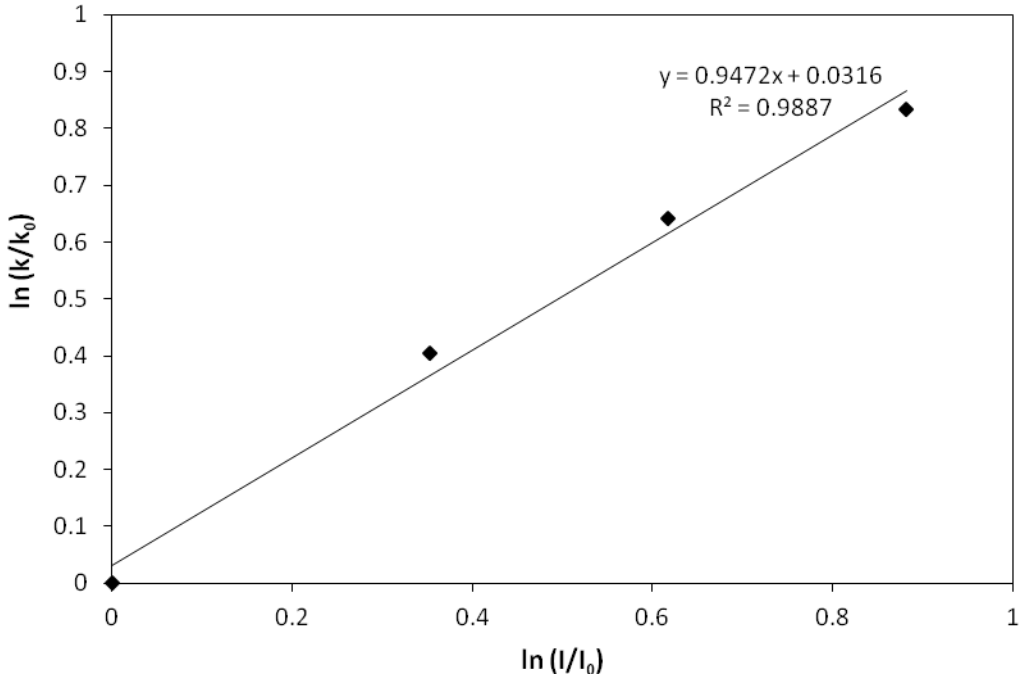


Figure 4.10: Plot of variation of apparent rate constant with UV intensity for the photocatalytic degradation of IPU

4.3.7 Effect of Area to Volume (A/V) Ratio of the Batch Reactor

While designing the reactor configuration for commercial applications, the depth of the solution is very critical for deciding the degradation. Generally, in photocatalytic treatment, less depth and more area is recommended so that light (UV or solar) can penetrate effectively in solution to be treated (Sharma et al., 2012). Surface area can be increased by keeping the volume constant and increasing the aperture or by keeping the aperture constant and decreasing the volume. In our study, we have kept the aperture constant and varied the volume of the solution. In the present study, the A/V ratio of the shallow pond reactor was varied from 0.59 to 1.77 cm^2 ml^{-1} and concentration data is shown in figure 4.11. The photocatalytic degradation rate for IPU increased with increase in aperture to volume ratio of the reactor (Fig. 4.12). With more A/V ratio, surface area of the solution is enhanced leading to increase in path length of photons entering the solution resulting in higher OH radical yield.

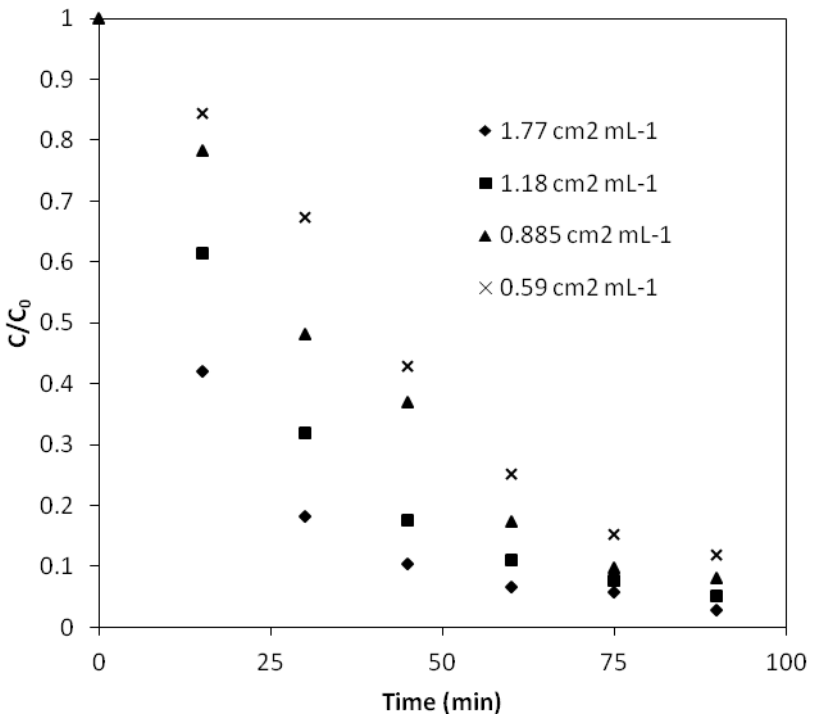


Figure 4.11: Effect of area/volume ratio for the degradation of IPU (TiO_2= 0.5gL^{-1}, C_0 = 25 mgL^{-1}, pH = 5.0, and UV intensity 23 Wm^{-2})

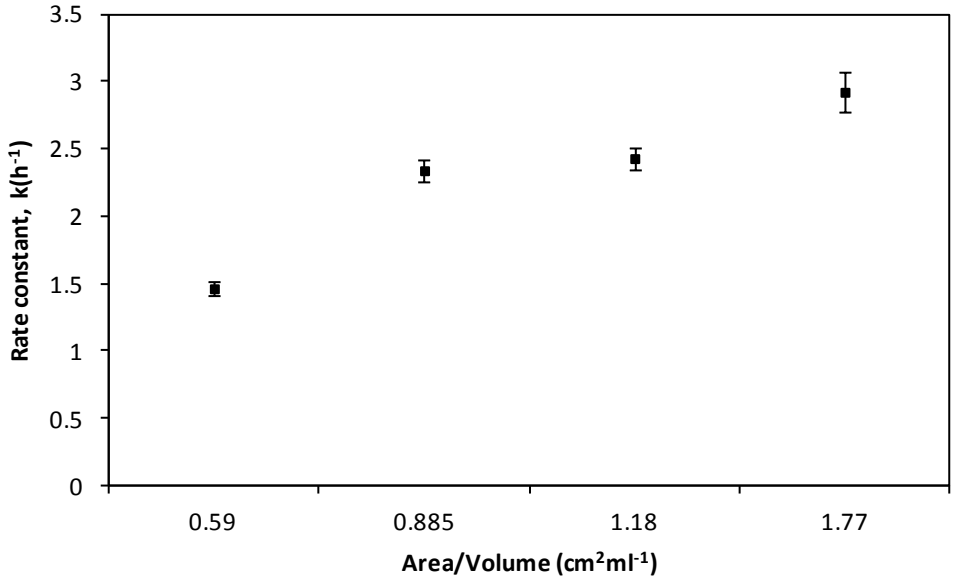


Figure 4.12: Effect of A/V ratio on the rate constant for the degradation of isoproturon

4.3.8 Catalyst Recycling

For the industrial applications of photocatalytic process in slurry mode, the recycling of the photocatalyst is very important component to reduce the cost implications. Catalyst lifetime is very important for deciding the cost concerns of the process. To understand this, catalyst recycling studies have been done and presented in Fig. 4.13. After each cycle, the photocatalyst was filtered and oven dried at 85^{o}C before being used again. In our case, the photocatalyst was recycled effectively for four times but with 12% reduction in the efficiency. The UV-VIS DRS spectra confirmed that band gap as well as wavelength excitations are not changed for fresh and used (after 4th cycle) catalyst (Fig. 4.14). The major reason behind the reduction in the degradation rate is catalyst fouling due to accumulation of the pollutant on the surface of the catalyst (Sharma et al., 2008a). The loss of small amount of catalyst during filtration can also be accounted for efficiency reduction.

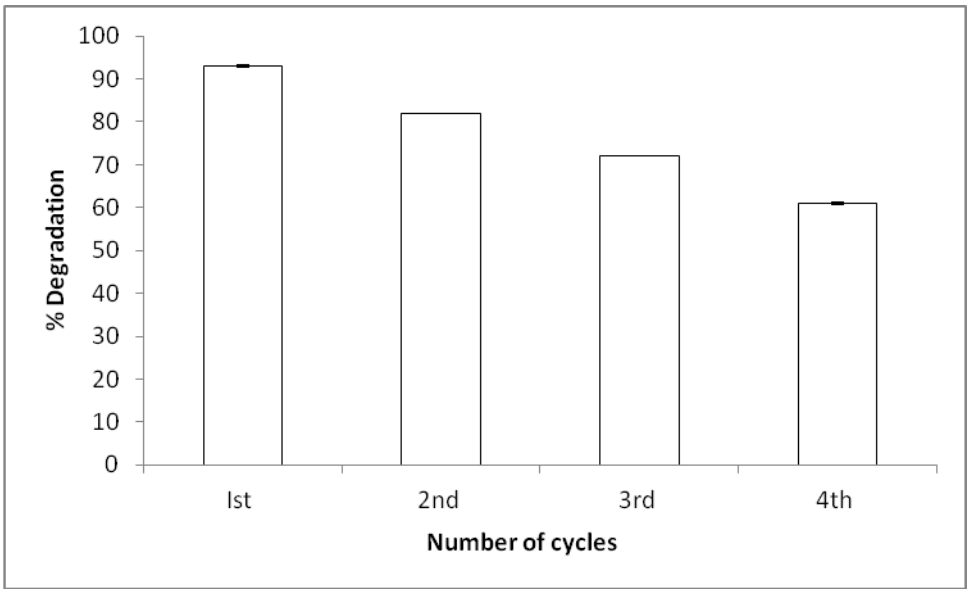


Figure 4.13: Catalyst recycling studies for the slurry mode during photocatalytic degradation of isoproturon

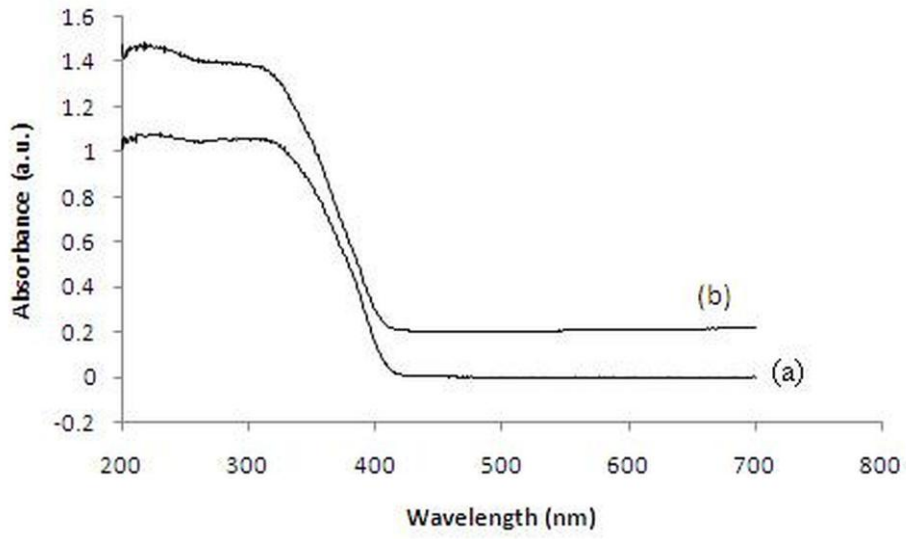


Figure 4.14: UV-VIS DRS spectra of (a) Fresh TiO_2 (b) recycled TiO_2 after 4th cycle for the degradation of isoproturon under UV irradiations (C_0 = 25 mgL^{-1}, pH =5.0, and UV intensity 23 Wm^{-2})

4.3.9 Fixed-bed studies for the degradation of IPU

An attempt was made to immobilize the catalyst on the inert support with the view of commercial applications. A glass sheet 18 x 10 cm was roughened with sand paper, washed with 10% nitric acid and subsequently dried. The appropriate amount of

catalyst slurry was taken according to area calculation in slurry batch reactor (0.5 gL^{-1}). Slurry was sonicated for one hour for the uniform dispersion of the catalyst. The catalyst was coated on the plate following protocol similar to dip and coating method (Ray and Beenackers, 1998). In brief, based on the concentration of the catalyst required per unit area, slurry was prepared and sonicated. This slurry was then coated on the glass sheet in the form of film. The coated plate was left in oven at 110^{o}C for overnight and washed in morning to remove loosely coated particles. The method was repeated twice for getting the uniform thickness of the catalyst. Similar method was adopted for the immobilization of the photocatalyst on the small cement slabs (3 x3cm) made in lab.

With the method described above, the immobilized reactor was operated in natural sunlight conditions in recirculation mode with minimum loss of catalyst (Fig. 4.15 a). For achieving maximum degradation the slope of reactor was adjusted, to maintain the flow rate of isoproturon. The degradation achieved was nearly 70% in case of glass coated reactor and 55% in case of immobilization on cement slabs (Fig.4.15 b). The degradation of Isoproturon was obviously less than the slurry mode due to the mass transfer limitations of the substrate, but the immobilized surface was recycled for at-least 10 times with negligible reduction in efficiency. With little modifications, the surface as well as reactor can be modified so as to boost the commercial applications of fixed bed photocatalysis.

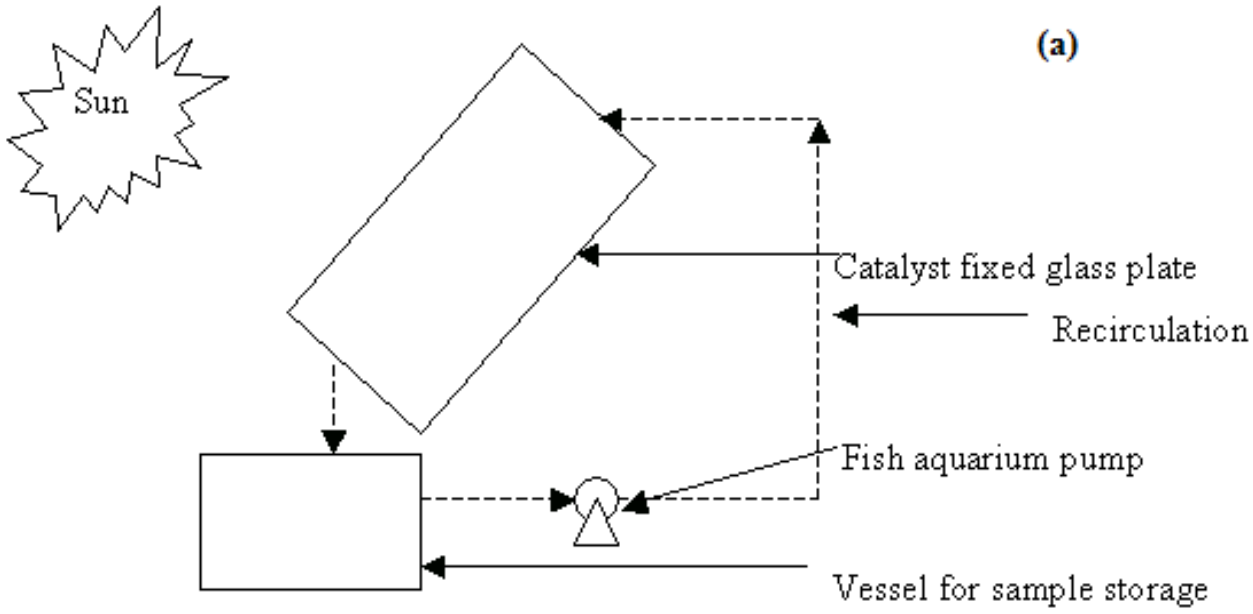


Figure 4.15. a: Schematic diagram for fixed bed photocatalysis

(b)

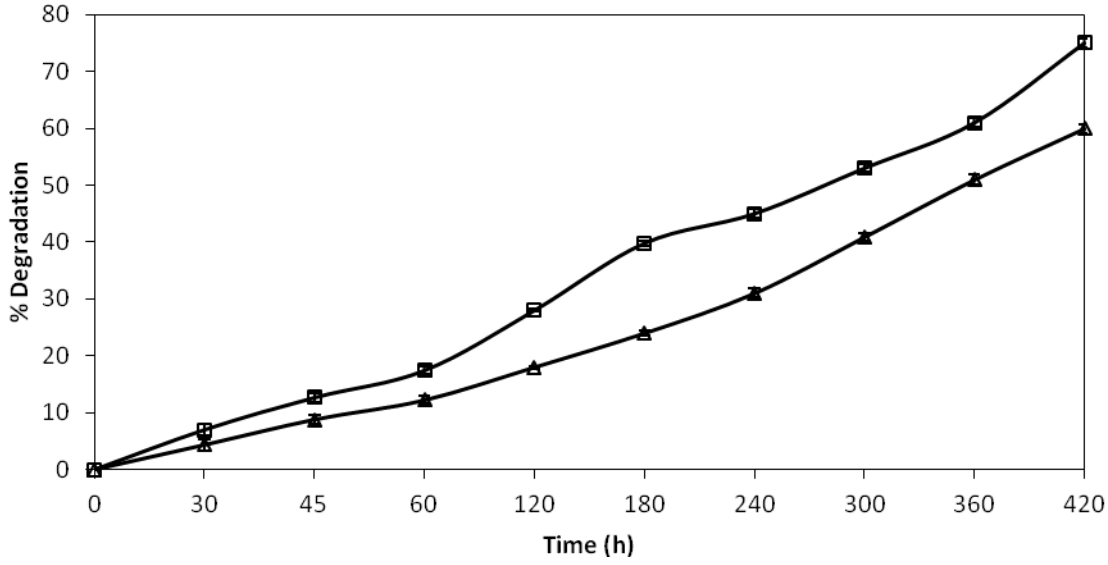


Figure 4.15 b: Fixed bed photocatalysis (i) □= glass sheet (ii) Δ= cement slab for the degradation of isoproturon under UV irradiations (C_0 = 25 mgL^{-1}, pH =5.0, and Solar UV intensity 23 Wm^{-2})

4.3.10 Mineralization Studies

Generally, complete photodegradation of the organic compound leads to the formation of CO_2 and various inorganic anions and cations (Evgenidou et al., 2005). In our study, the extent of mineralization was studied in terms of COD reduction along with the ammonium ions generation. The 96% reduction of COD of the isoproturon was observed after 2 h of irradiation during which release of ammonium ions was maximum. The monitoring of ammonium ions showed a rapid increase in initial 30 min of irradiation (77%) reaching a constant value (88%) after 2 h of photocatalytic treatment under optimized conditions as depicted in Fig. 4.16. The LC-MS analysis of the intermediate and final samples was performed to confirm about the status of intermediate products. The spectra confirmed the diminishing of parent compound along with the generation of some intermediates. The LC-MS analysis showed the presence of major intermediate product as monodemethylisoproturon (product 3) during the course of reaction given in table 4.1. This product was subsequently mineralized as confirmed by response time of chromatograms of LC-MS data of treated sample (Appendix). Similar intermediates identified for the above study have also been reported earlier (Haque and Muneer, 2003; Amorisco et al., 2005). On the basis of these identified intermediates, a pathway to complete mineralization is suggested shown in Fig. 4.17.

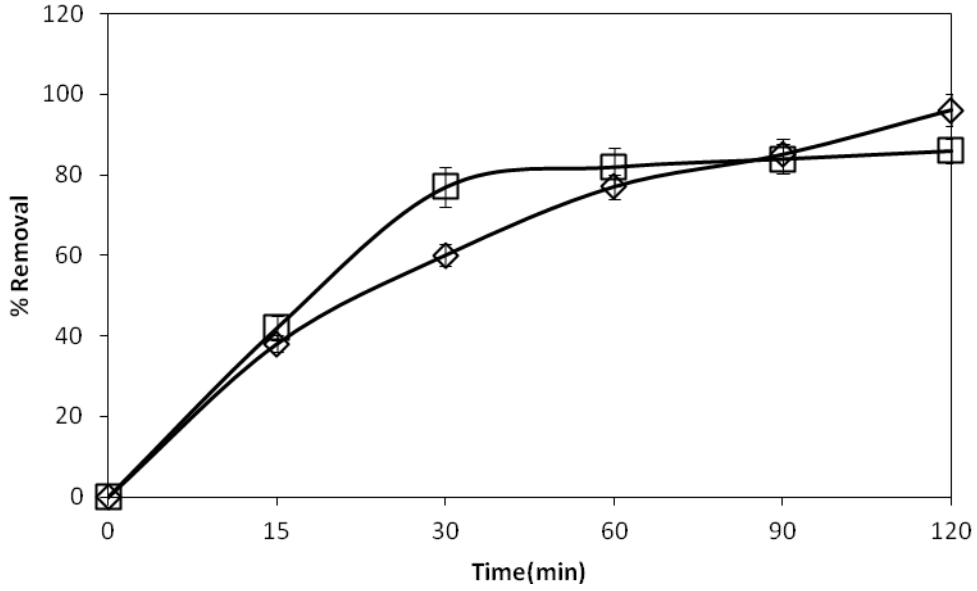


Figure 4.16: COD reduction (□) and ammonium ion (◊) generation during the photocatalytic degradation of isoproturon

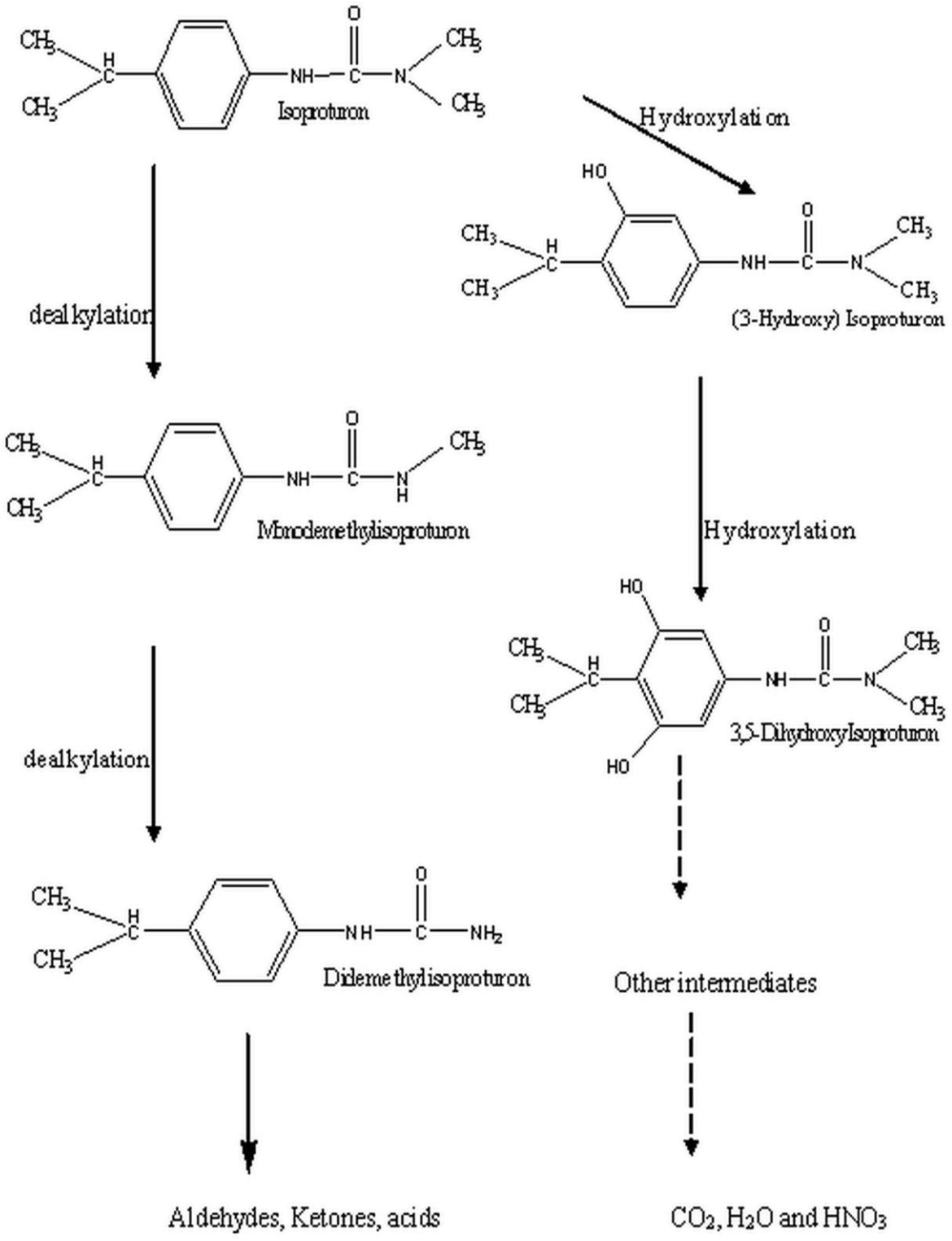
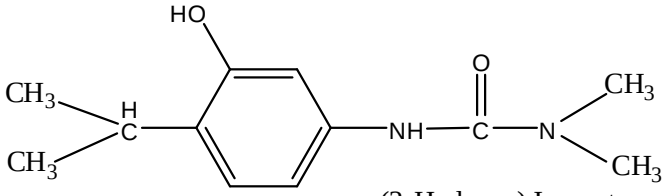
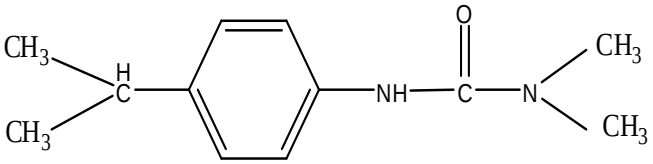
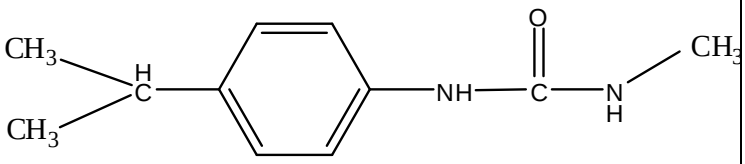
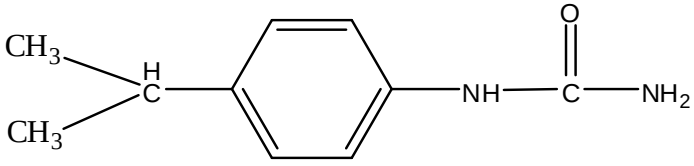


Figure 4.17: Predictive pathway for photocatalytic degradation of isoproturon (Sharma et al., 2008b)

Table 4.1: Mass spectra data for study of intermediates during photocatalytic degradation of isoproturon by LC-MS

S.No.	Compound name	t_r(min)	m/z ratios of main MS/MS fragments
1.	 (3-Hydroxy) Isoproturon	6.23	223,205, 181, 165, 73
2.	Isoproturon 	8.12	207,165, 134
3.	Monodemethylisoproturon 	7.51	193,151, 136
4.	Didemethylisoproturon 	6.95	179,162, 144, 134, 119

4.4 Photocatalytic degradation of herbicide Isoproturon using TiO_2 coated cement beads: Overview

This section deals with the degradation of isoproturon using spherical beads of cement and sand coated with TiO_2 (as discussed in section 3.6.2). Photocatalytic degradation using coated beads was optimized by varying operating parameters like number of catalyst coatings, UV intensity, bead diameter, calcination temperature etc. and the intermediate products were identified through LC-MS analysis along with the mineralization studies.

4.4.1 Preliminary Studies

Blank experiments were performed using bare cement beads (without TiO_2 coating) in a UV light using batch reactor. A negligible photodegradation was observed owing to photolytic activity and adsorption on the bare beads. Moreover, adsorption studies on TiO_2 coated beads in dark confirmed 8% reduction in concentration of IPU after 3 h of irradiations (Fig. 4.18). This loss in concentration is mainly due to the formation of monolayer of the IPU on the catalyst surface. Actually after the monolayer formation, no free active sites on the catalyst would be available and therefore no further reduction in concentration was observed (Toor et al., 2007). The use of oxidant (H_2O_2) alone contributed to 4% degradation due to small amount of OH radicals produced. The combination of all i.e. UV + TiO_2 coated beads showed 90% degradation after 5 h of illumination, thus leading to an assumption that adsorption-desorption of the IPU and reaction intermediates are relatively slow as compared to the formation of electron/hole pairs (Haque and Muneer, 2003). In contrary, more than 90% degradation of IPU was achieved in slurry TiO_2 mode after 3 h of irradiations due to high mass transfer between pollutant and active sites of catalyst. Although the

degradation of IPU is more effective in slurry mode however the separation of catalyst is not feasible.

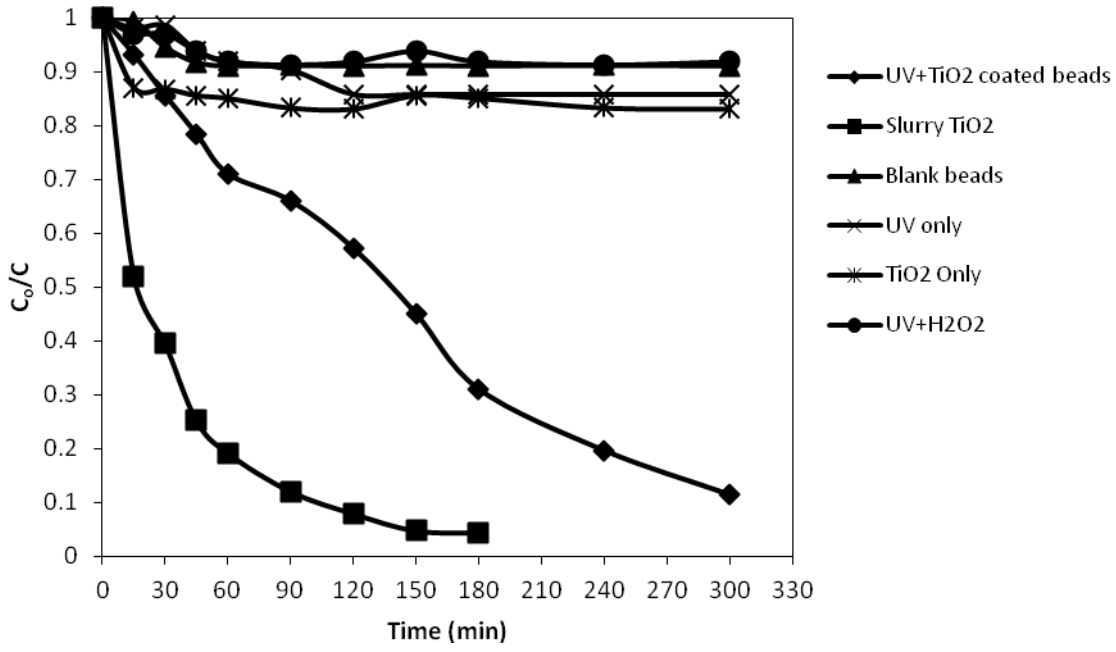


Figure 4.18: Photolysis, photocatalytic reduction of Isoproturon in the presence and absence of TiO_2 along with adsorption and slurry TiO_2 studies. Experimental conditions: 25 mgL^{-1} isoproturon, V= 200 ml, UV intensity = 23 Wm^{-2}

4.4.2 Photocatalysis using immobilized cement beads: Effect of number of coatings

The stable and thick layer of TiO_2 on the support material would be required for effective degradation of IPU. With each cycle of coating, the thickness of TiO_2 layer was formed on the surface of cement bead depending upon its size and texture. Further increase in number of coatings on the surface, the catalyst particles were loosely bound and were susceptible to detachment from the immobilized surface. This will additionally obstructs the path of light penetrating the solution leading to the scattering of light by increasing the concentration of TiO_2 in solution. In this context, the effect of number of TiO_2 coatings on the beads were studied for the photocatalytic degradation studies for isoproturon. It was observed that the degradation was only 65% if the TiO_2 was coated once over the beads. When the number of coatings of the photocatalyst was

increased from 2 to 4 times, the herbicide degradation stabilized after second coating and continued to remain nearly same till 4th coating. Degradation was close to 90% in each of these cases after 5 h of treatment (Fig. 4.19). Further it was concluded, two numbers of coatings were came out be optimum for the degradation of IPU.

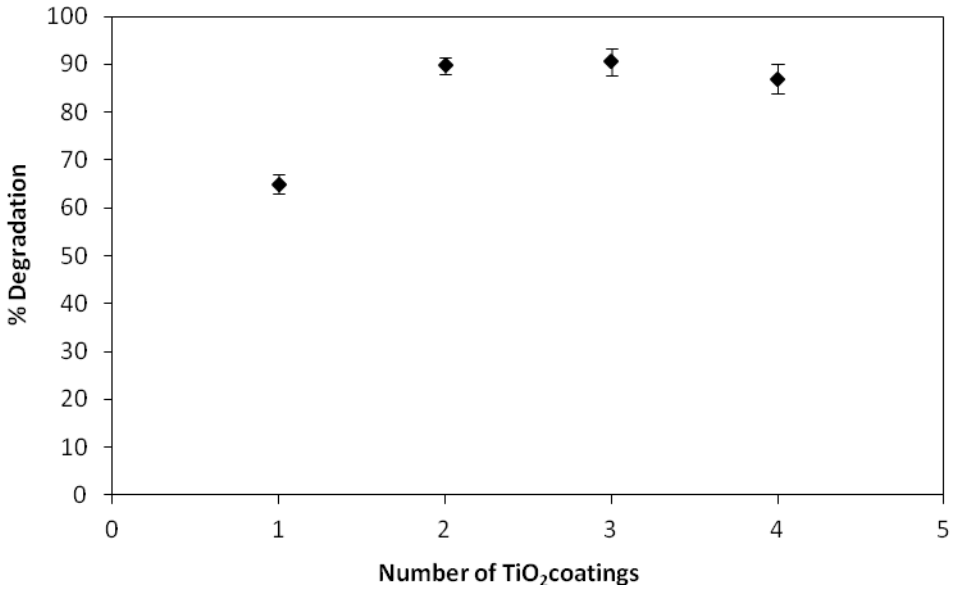


Figure 4.19: Effect of number of TiO_2 coatings on cement beads for photocatalytic reduction of Isoproturon. Experimental conditions: 25 mgL^{-1} isoproturon, V= 200 ml, UV intensity = 23 Wm^{-2}

4.4.3 Effect of bead size

The available surface area for the reaction in any liquid-solid system plays vital and promising factor for its commercial applications. In photocatalytic degradation process, more exposed area is preferred as more solar radiations can be utilized. Hence we have studied the degradation of isoproturon by varying the average surface area of the cement beads. In this context, spherical cement beads of different sizes have been made and tested them for photocatalytic activity after immobilizing the catalyst. Cement beads size was varied from 1.0 cm to 2.5 cm and TiO_2 was immobilized using method discussed in chapter 3. The diameter of bead is taken as average value of the diameter of 50 beads and at different locations. As the average diameter of cement bead

increases, the degradation of isoproturon decreases from 90% to 80% owing to the decrease in effective surface area available (Fig. 4.20). The catalyst is not effectively immobilized with beads of very small diameter i.e. < 1cm average, thus didn't yield very good degradation probably due to very small surface available for coating.

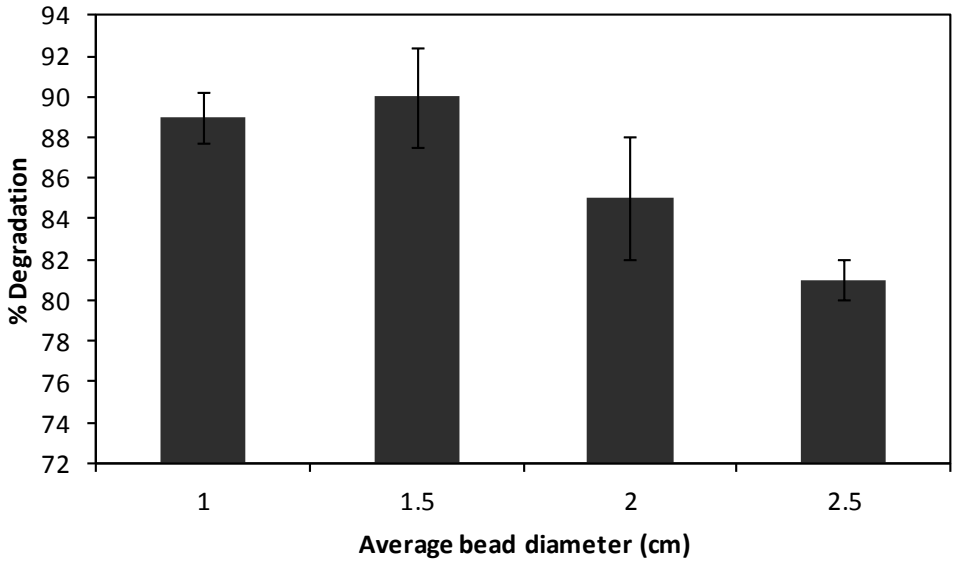


Figure 4.20: Percentage degradation data of isoproturon (C_o=25 mgL^{-1}) for varying average diameter of TiO_2 coated cement bead with UV intensity 23 Wm^{-2}

4.4.4. Effect of calcination temperature

Heat treatment influences the specific surface of the photocatlyst along with affect on the surface defects and active sites (Shifu and Gengyu, 2005). The catalyst stability on the support is also strongly dependent on the heat treatment during the immobilization process. Thus efforts have been made to calcine the cement beads, after the TiO_2 coating, at different temperatures i.e. 200, 300 and 400 ^oC for 2 h. The photocatalytic activity of beads calcined at different temperatures was determined by degradation efficiency of isoproturon. It was evident that the degradation efficiency was better when the beads are calcined at 400 ^oC than at lower temperature (table 4.2). Actually the stability of the coating was point of concern at high temperatures as increase in calcination temperature did not enhance the degradation rate.

Table 4.2 : Photocatalytic activity of cement beads at different muffle temperatures

T (^oC)	200 ^oC	300 ^oC	400 ^oC
Degradation Efficiency (%)	64±5	73.5±4.5	90±6.5

4.4.5 Effect of H_2O_2 addition

The degradation rate of the organic pollutants is significantly affected by addition of the various electron acceptors like hydrogen peroxide. The role of hydrogen peroxide for enhancing the photocatalytic degradation rates is now well established. At lower H_2O_2 dosages, the rate improvement is probably due to generation of OH radicals by direct photolysis of H_2O_2 in sunlight. Also, it facilitates the electron-hole recombination, according to the equation 4.5 (Cornish et al., 2000):

$$TiO_2 (e-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^\cdot \quad (4.5)$$

In general, H_2O_2 accepts the photo-generated electron from the conduction band and thus promotes the charge separation, and thereby forming OH radicals. In our study, H_2O_2 was varied from 0.25 ml to 1.0 ml in photodegradation of IPU and addition had synergistic effect as degradation increased to 90% after 4h of treatment at 0.5ml optimum dose as shown in figure 4.21. However overdose of H_2O_2 retards the isoproturon photocatalytic rates as high concentration of H_2O_2 acts as a scavenger (Malato et al., 2009).

The OH radical quenching at excess hydrogen peroxide might be the reason behind low degradation rates. Actually, when hydrogen peroxide concentration is high, the amount of OH radical formed on the surface of the catalyst increases rapidly and

hence the annihilation (OH• + OH• → H_2O_2) rate is much faster than the reaction rate of OH radical and organic contaminants. Hydroxyl radicals are annihilated before the reaction of OH radical with organic contaminants. At high concentration of H_2O_2, it acts as a scavenger as shown in the following equations, 4.6 & 4.7 (Verma et al., 2014):

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (4.6)$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + O_2 \quad (4.7)$$

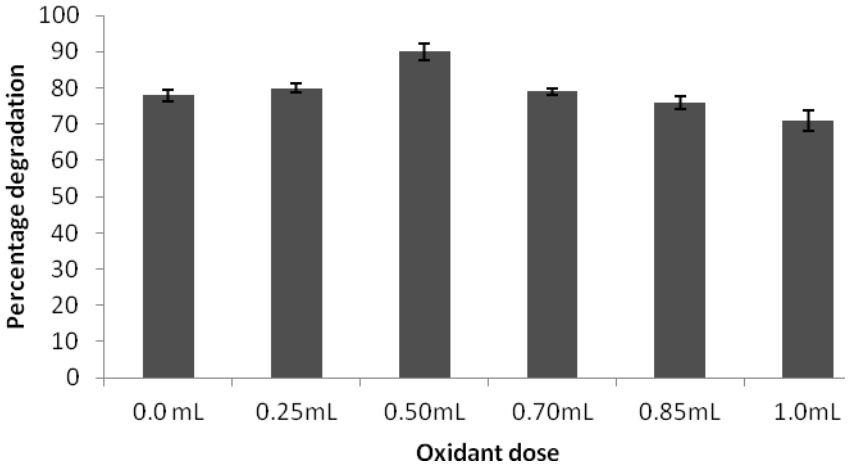


Figure 4.21: Effect of varying H_2O_2 concentration on the photocatalytic degradation of isoproturon (C_0 = 25 mgL^{-1}, UV intensity = 23 Wm^{-2}, average bead diameter=1.5cm)

4.4.6 Effect of UV intensity

The intensity of UV radiations varies throughout the year in solar conditions. The UV intensity plays very important role for field scale applications of AOP. In this view, the intensity of UV radiations was varied using UV-radiometer from 10 to 25 Wm^{-2} in chamber keeping the aperture to volume constant. It was concluded, that degradation of isoproturon increases from 60% to 90% as the intensity of UV radiations varies from 10 to 25 Wm^{-2} (Fig. 4.22). With the increase in intensity of light, actually number of OH radicals is increasing leading to enhancement of degradation rate (Verma et al., 2013).

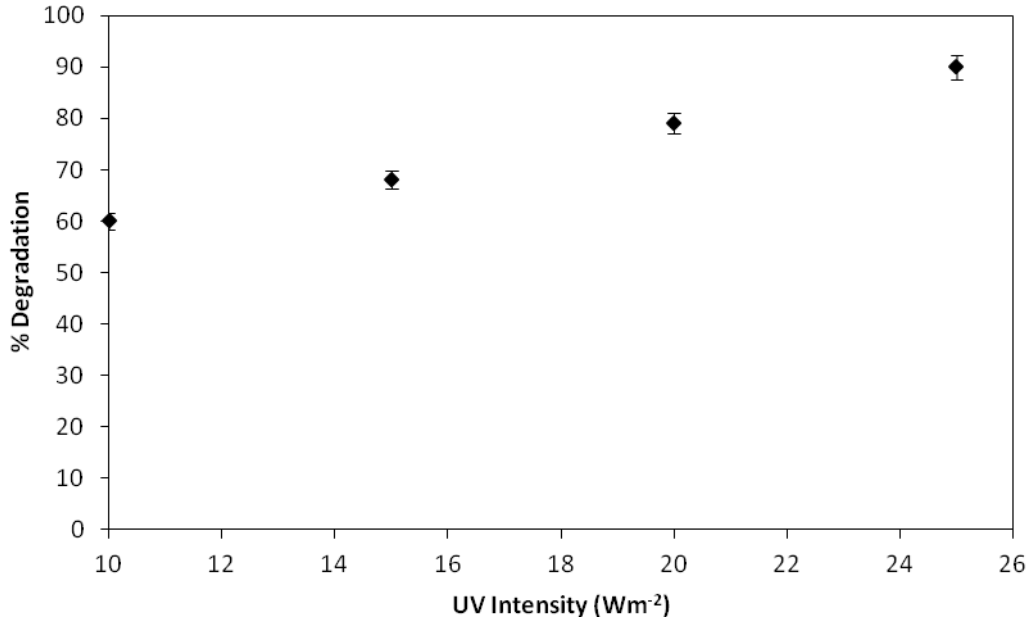


Figure 4.22: Percentage degradation versus variation in UV intensity during photocatalytic degradation of isoproturon (C_0 = 25 mgL^{-1})

4.4.7. Durability studies

The main implication in the studies of fixed-bed catalysis is durability of the supported catalyst, thus limits its viability of commercial applications. Although, number of supports has been studied in literature but, the supported catalyst activity is reported to be reduced after six runs (Parra et al., 2004). The re-activation of the supported catalyst requires heat treatment at high temperatures (480 ^{o}C), which is generally not viable from economic point of view. In this view, present study deals with efforts for checking the durability of the immobilized catalyst on cement beads for the degradation of the isoproturon. In our study, the beads were effectively recycled for at-least thirty times with little reduction in efficiency in context to degradation of isoproturon (Fig. 4.23). To best of our knowledge, this is first reported study of number of recycling (to the extent of thirty times) for the degradation of herbicide isoproturon or any other compound. Fig. 4.24 presents actual images of the coated cement beads

during various stages of recycling, which show that coating is intact even after 30th cycle, hence can also be further used as such. The SEM image shows the morphology of recycled beads and micrograph is presented in fig. 4.25. From SEM images and EDAX analysis, it is clear that catalyst is intact even after 30th recycle confirming its stability. After each cycle, the catalyst coated cement beads were exposed to solar radiations for 1-2 h otherwise oven heated at 100 ^{o}C for one hour for reactivation.

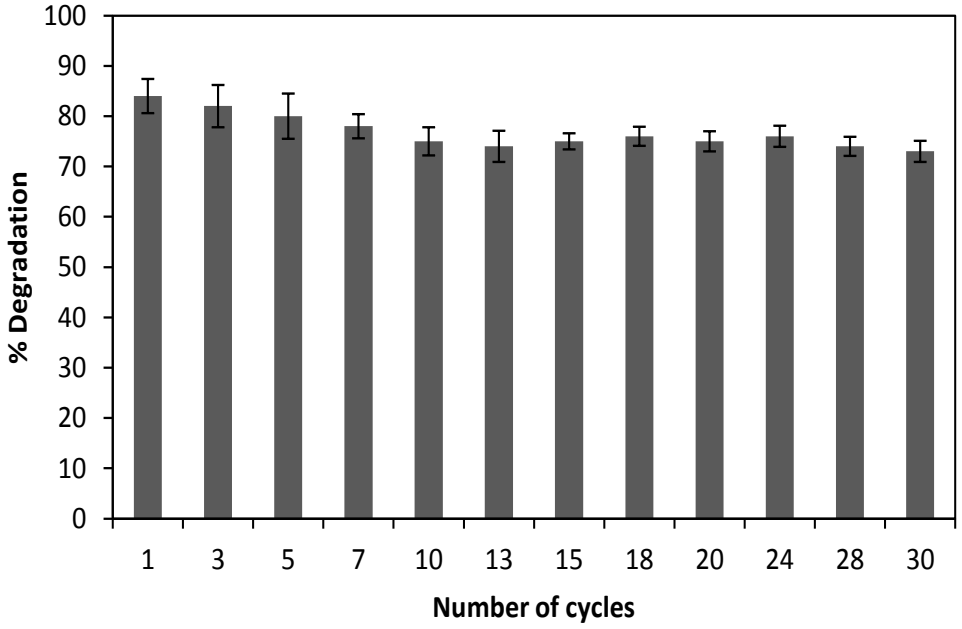


Figure 4.23: Recycling studies for the photocatalytic degradation of isoproturon (C_0 = 25 mg L^{-1}, UV intensity = 23 W m^{-2}, average bead diameter = 1.5 cm)

Beads were also given heat treatment in muffle furnace at 400 ^{o}C for 1 h for confirmations and results were crosschecked. No significant change in the percentage degradation of isoproturon was recorded thus proposing the re-activation at lower temperatures.

Figure 4.24: Images of TiO_2 coated cement beads (a) Original coating (b) After 5th recycle (c) After 15th recycle (d) After 30th recycle for the degradation of herbicide isoproturon

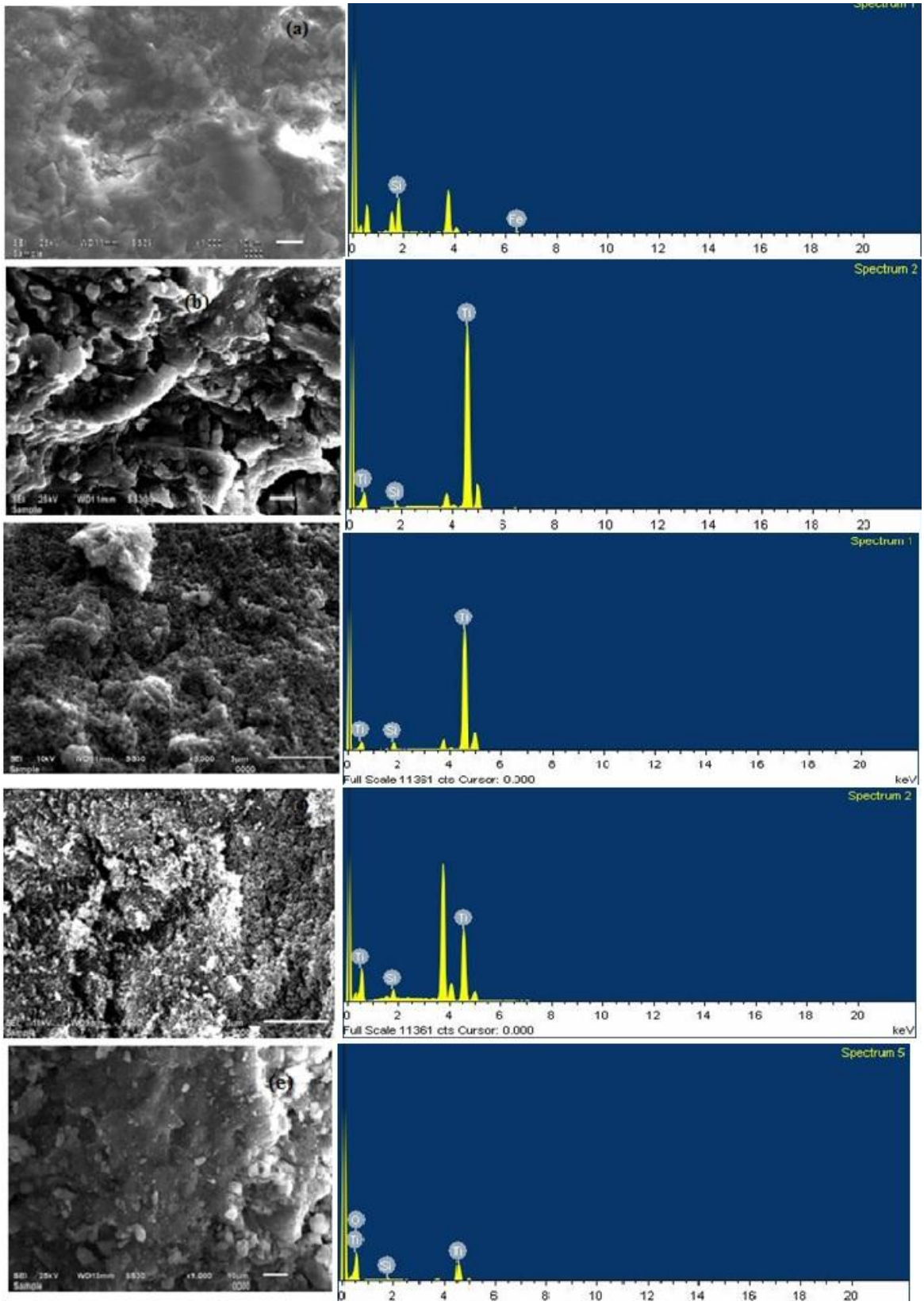


Figure 4.25: SEM photographs of (a) Bare cement beads without TiO_2 coating (b) Fresh coated TiO_2 (c) After 5th recycle (d) 15th recycle (e) 30th recycle along with corresponding EDAX measurements

4.4.8 Solar Fixed bed baffled reactor studies

A fixed bed baffled reactor (FBBR) was designed employing above mentioned cement beads and used for studying the degradation of isoproturon in under natural sunlight conditions (Section 3.6.4.1). The average solar and UV intensity was 600 and 28 W m^{-2} respectively (measured from 10.00 AM to 4.00 PM) with surrounding temperature 30 ± 4 ^{o}C. The cement beads coated with TiO_2 were used in proportion to area calculations to that of lab scale reactor. The sufficient depth of the FBBR was maintained to submerge the catalyst coated beads. The FBBR was operated in recirculation mode with flow rate maintained at 0.5-1.0 L min^{-1}. The 85% degradation of isoproturon was observed after 6 h of treatment (Fig 4.26). The FBBR was checked for its durability as recycling studies were performed, where the same set-up was used for another twenty batches for studying degradation of isoproturon. Mainly, attrition of catalyst is a problem observed in flow systems but in our case, we had a negligible attrition as confirmed from constant degradation data. Further the design of the reactor can be modified, where treatment time can be reduced by increasing the retention time of solution in FBBR. With these modifications, along with studied immobilized surface, reactor can boost the commercial applications of fixed bed photocatalysis.

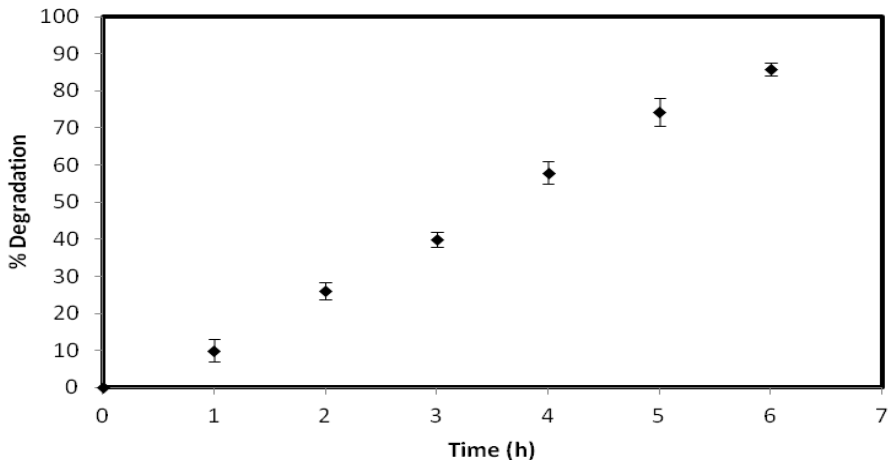


Figure 4.26: Degradation of isoproturon under solar irradiations (C_0 = 25 mg L^{-1}, and average solar UV intensity 23 W m^{-2}, average bead diameter=1.5 cm)

4.4.9 Mineralization studies

For practical applications, the properties of intermediate and mineralization products are very important aspect for photocatalytic treatment. The mineralization studies of IPU have been carried out in terms of TOC reduction along with NH_4^+ generation. In our study, we have achieved 92% reduction in COD and 90% reduction in TOC after 5 h of photo-treatment of IPU during which release of ammonium ions was maximum. Under optimized conditions, the release of NH_4^+ ions reached 65% during first 2 h of treatment and subsequently reached to constant value of 80% after 5 h of treatment (Fig. 4.27).

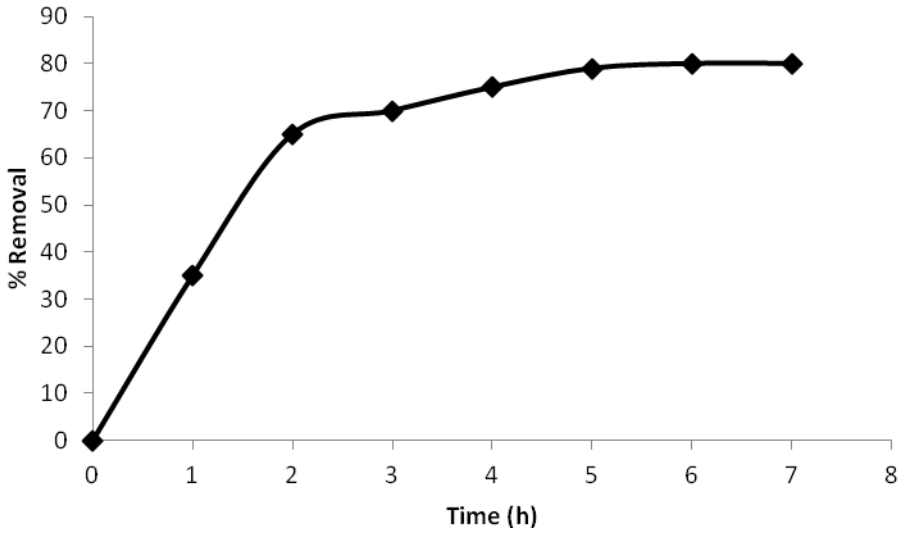


Figure 4.27: NH_4^+ generation during the photocatalytic degradation of isoproturon using TiO_2 coated cement beads

The LC-MS analysis of the treated sample confirmed the formation of various intermediates viz. (i) monodemethylisoproturon (ii) didemethylisoproturon (iii) 3-hydroxy isoproturon during photocatalytic degradation of isoproturon (Table 4.3), as reported in our previous studies.

Table: 4.3. Details of the Metabolites name with transitions

S.No.	Intermediate	Treated	Transitions
1	Monodemethylisoproturon	-	193>94,136,151,193
2	Didemethylisoproturon	Didemethylisoproturon	179>91,106,119,134
3	3-Hydroxyisoproturon	3-Hydroxyisoproturon	223>134,165,181,205

4.5 Photocatalytic degradation of insecticide Imidacloprid under UV and solar irradiations: slurry and fixed-bed photocatalysis

4.5.1 Standard calibration curve of imidacloprid

The absorbance of imidacloprid solution was studied between the wavelength of 200 to 800 nm and maximum absorbance (λ_{max}) was obtained at 269 nm. Standard concentrations of imidacloprid were prepared from 5 mgL^{-1} to 25 mgL^{-1} and their absorbance at 269 nm was measured.

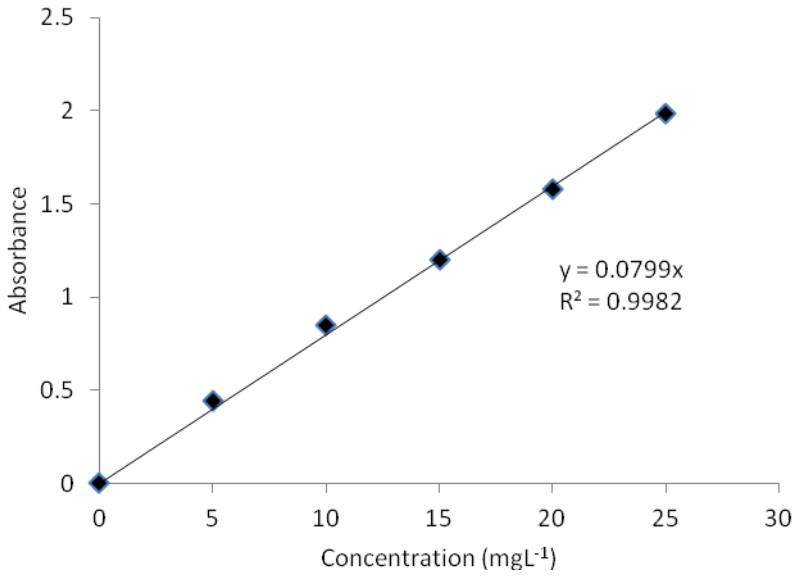


Figure 4.28: Standard curve of insecticide imidacloprid

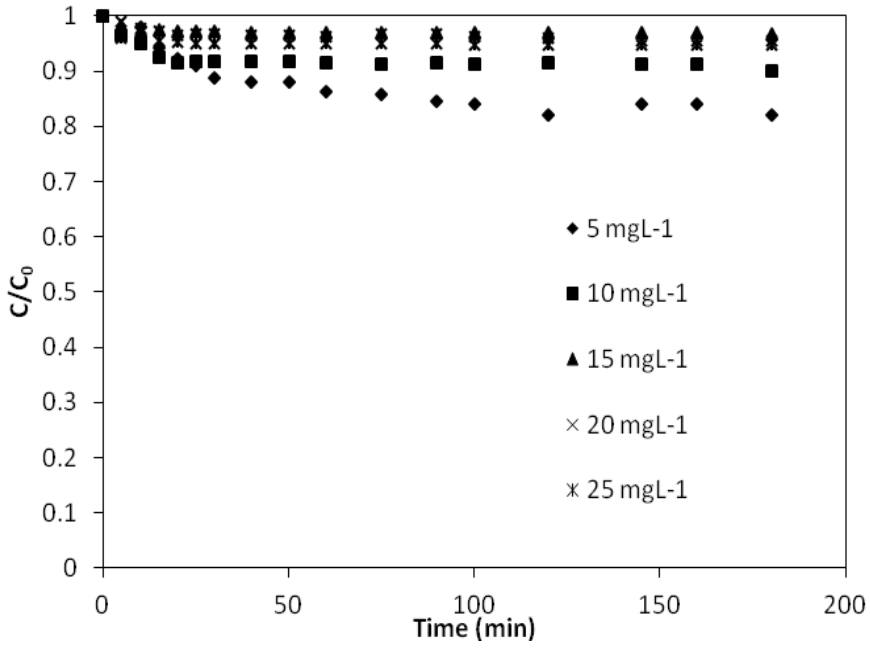
A graph of absorbance vs. various standard concentrations of imidacloprid was plotted (figure 4.28). Regression coefficient was found to be 0.9982 and slope was 0.0799. From this calibration curve, unknown concentration for imidacloprid solution can be calculated.

4.5.2 Photolytic and Adsorption Studies

For the photocatalytic reactions, both catalyst and a light source are required for the photo-oxidation reaction to occur. In this context, adsorption and photolytic studies were performed as control experiments prior to photocatalytic experiments. The

imidacloprid solution of varying concentrations was kept in dark with TiO_2 for 200 min and no degradation was observed (fig. 4.29 a). To the 200 ml of imidacloprid solution, 0.2 mg of catalyst was added and allowed for stirring in the dark. Aliquots were withdrawn after every 15 min and the change in concentration was monitored. The decrease in concentration of imidacloprid corresponded to extend of adsorption (6-7%), whereas maximum adsorption was reached within 30 min. There was no significant change in concentration of imidacloprid even after three hours. The loss in concentration is mainly due to the formation of monolayer of the insecticide on the catalyst surface. After the monolayer formation, no free active sites would be available and therefore no further reduction in concentration was observed. From the results, it can be concluded that adsorption equilibrium was established within first 30 min and remained as optimum equilibrium time for all the photocatalytic experiments.

(a)



(b)

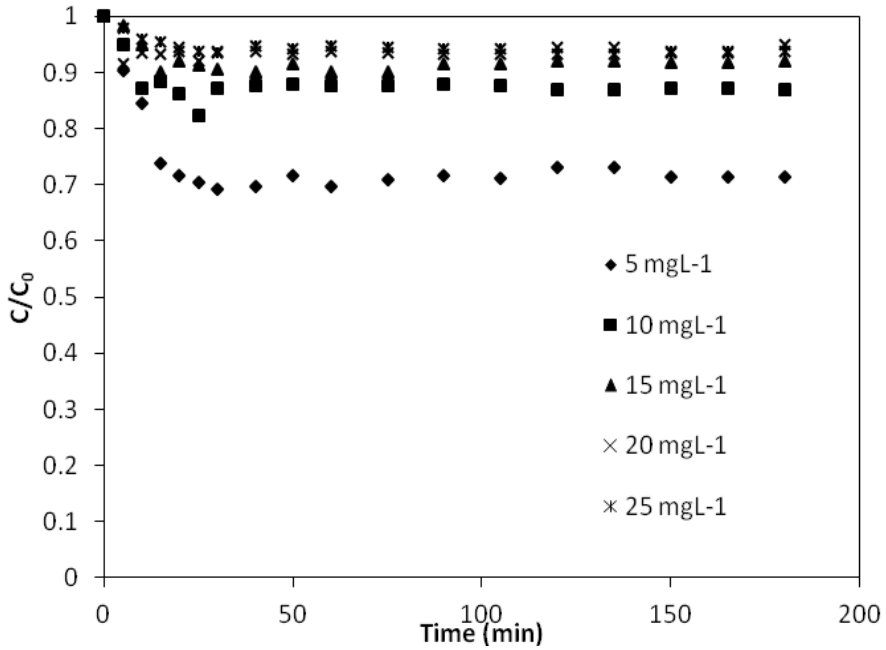


Figure 4.29 (a) Adsorption and (b) photolytic studies of insecticide imidacloprid at different initial concentrations. Experimental conditions: V= 200 ml, UV intensity = 23 Wm^{-2}.

The photolysis experiments (without TiO_2) were also conducted by irradiating 200 ml of imidacloprid solution under only UV/solar light over a period of 180 min in the batch reactor (Fig. 4.29 b). The study confirmed negligible photodegradation (6%) of the compound thus describing that the degradation observed in the presence of catalyst is due to catalyst activity. The photocatalytic treatment showed 95% degradation, thus leading to an assumption that adsorption-desorption of the pesticide and reaction intermediates are relatively slow as compared to the formation of electron/hole pairs (Verma et al., 2013).

4.5.3. Effect of Photocatalyst Concentration

TiO_2 dose was varied from 0.5 to 3.0 g L^{-1} to understand the effect of photocatalyst concentration on the degradation kinetics of the imidacloprid (Fig. 4.30). As the dose was varied from 0.5 to 1.0 g L^{-1}, the photocatalytic reaction rate constant

increased and activity was reduced with further catalyst dose. With large number of catalyst particles, number of photons absorbed in UV light increases thus leading to increase in the rate. Higher dose after the optimum increases the turbidity of solution, resulting in lesser penetration of light in solution that leads to reduction of hydroxyl radicals. At higher concentration, the particles of TiO_2 aggregates, causing a decrease in the number of active sites on its free surface leading to reduction in surface area and thus photocatalytic rate. Economically, also it is not recommended for higher concentration of TiO_2. Fig.4.31 shows a plot of the first-order rate constant (k) as a function of the catalyst concentration.

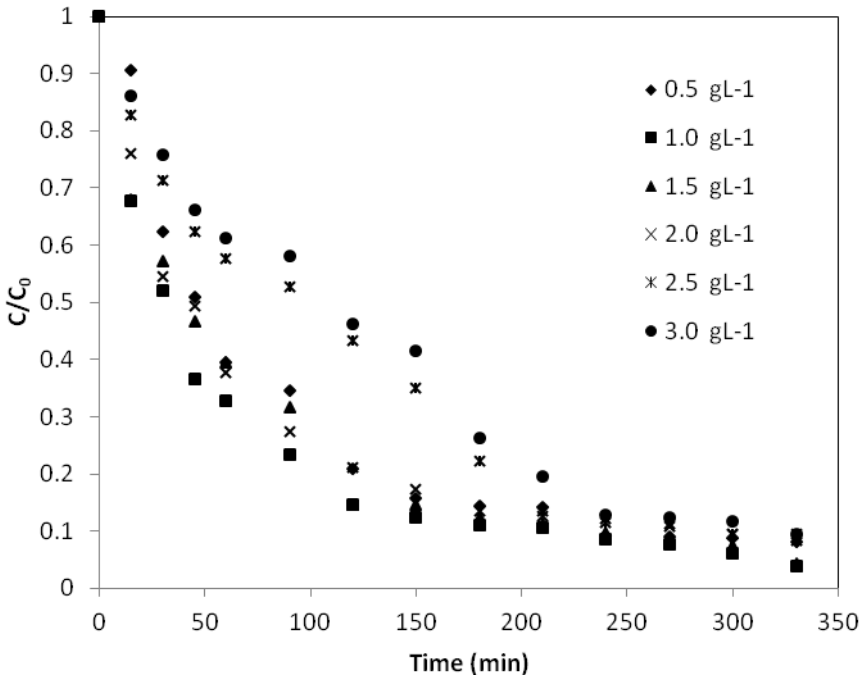


Figure 4.30: Degradation of imidacloprid with varying concentrations of photocatalyst TiO_2 using slurry batch reactor (C_0 = 25 mgL^{-1}, reaction volume = 200 ml, and UV intensity 23 Wm^{-2})

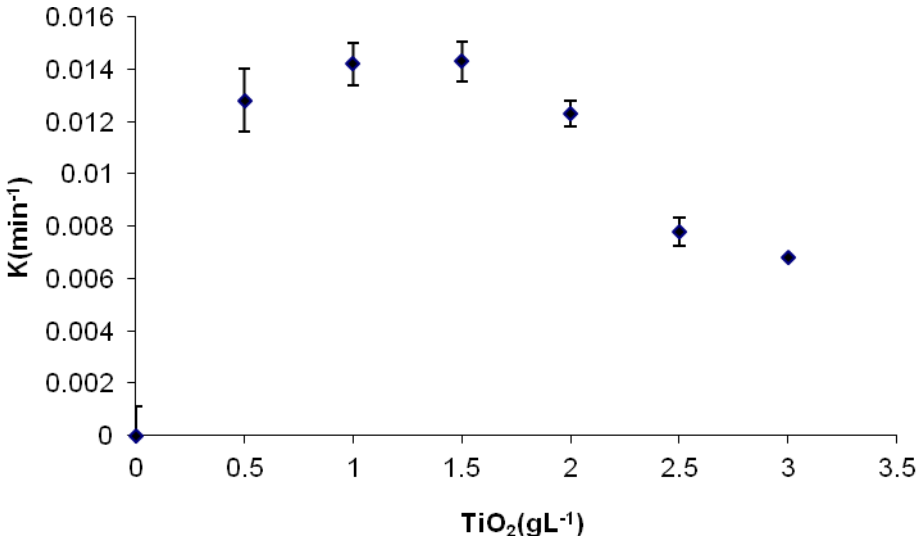


Figure 4.31: Effect of catalyst concentration on the rate constant during photocatalytic degradation of imidacloprid

4.5.4 Effect of oxidant addition

Oxidant like hydrogen peroxide (H_2O_2) enhances the photocatalytic degradation rate by accepting a photo-generated electron from a conduction band and thus promotes the charge separation, and it also forms OH• radical, according to Eq. 4.8. However, it acts as a scavenger at high concentration as shown in Eqs. 4.9 and 4.10. Therefore, determination of optimum concentration of hydrogen peroxide experimentally is needed.

$$TiO_2 (e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + \bullet OH \quad \textbf{(4.8)}$$

$$H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O \quad \textbf{(4.9)}$$

$$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2 \quad \textbf{(4.10)}$$

In this study, H_2O_2 concentration was varied from 0.15 to 0.75 gL^{-1} for the photocatalytic degradation of imidacloprid with optimum catalyst dose of 1.0 gL^{-1} at 23 W m^{-2} UV intensity (Fig. 4.32). It is clear from Fig. 4.33 that the rate of degradation

goes on increasing with the increase in concentration of H_2O_2 upto 0.3 gL^{-1} and then starts decreasing with further increase in concentration of H_2O_2.

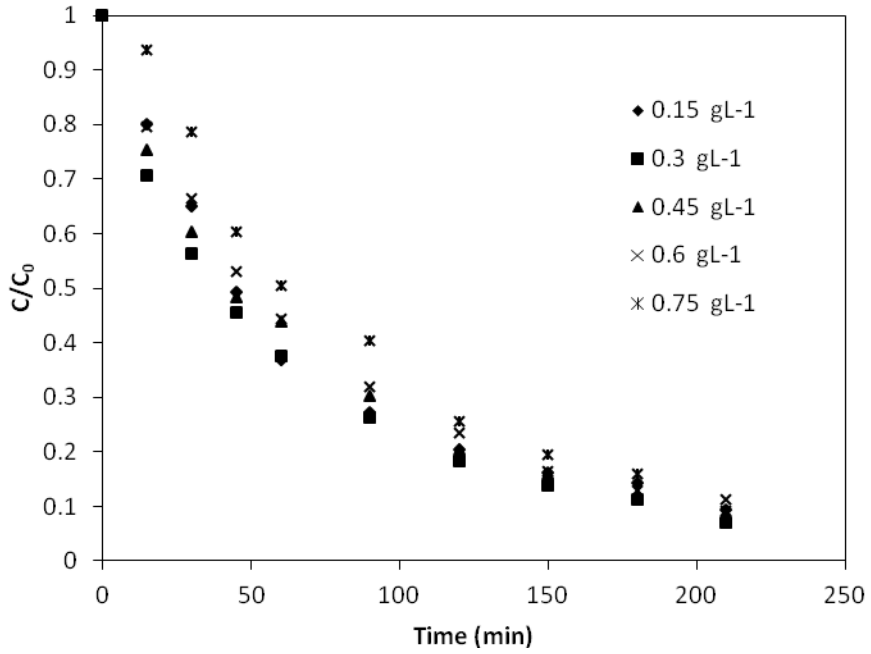


Figure 4.32: Concentration data for the effect of H_2O_2 addition on the degradation of herbicide IPU (TiO_2= 1.0 gL^{-1} , UV intensity = 23 Wm^{-2} , C_0 = 25 mgL^{-1})

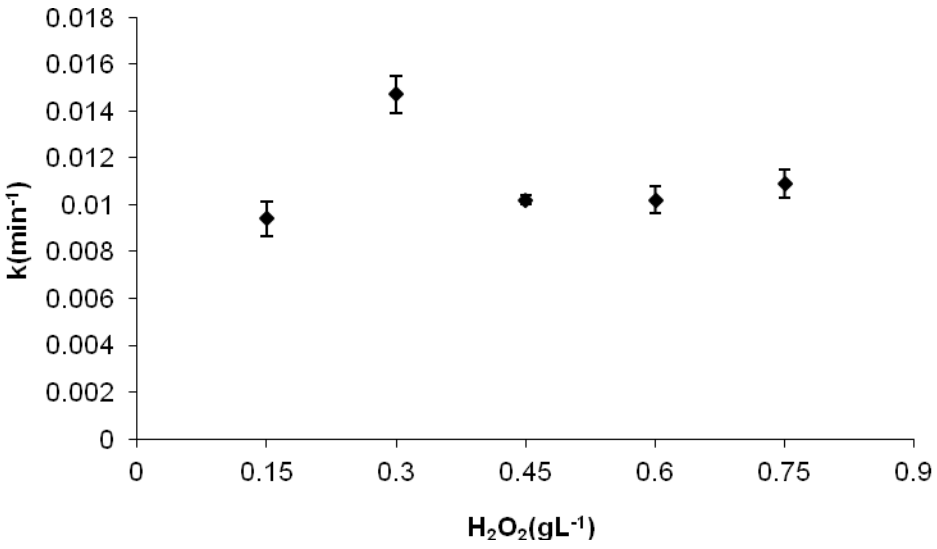


Figure 4.33: Effect of varying H_2O_2 concentration on the photocatalytic degradation of imidacloprid

4.5.5 Effect of initial concentration of imidacloprid

As discussed in section 4.3.4, the effect of initial concentration of pollutant is an important parameter from an application point of view to study its removal efficiency. Similarly, in this study the imidacloprid concentration was varied from 5 – 30 mg L^{-1} with optimum catalyst dose of 1.0 gL^{-1} at H_2O_2 dose of 0.3 gL^{-1} (Fig. 4.34). The photocatalytic degradation rate is first order at lower substrate concentration and becomes zero order at higher concentrations as per Langmuir-Hinshelwood (L-H). As the initial concentration of imidacloprid was increased to 25 mg L^{-1}, the degradation rate became constant thereafter (Kitsiou et al., 2009). The production of OH radicals by the catalyst is not sufficient in comparison with amount of insecticide adsorbed on the surface of the photocatalyst at higher concentrations.

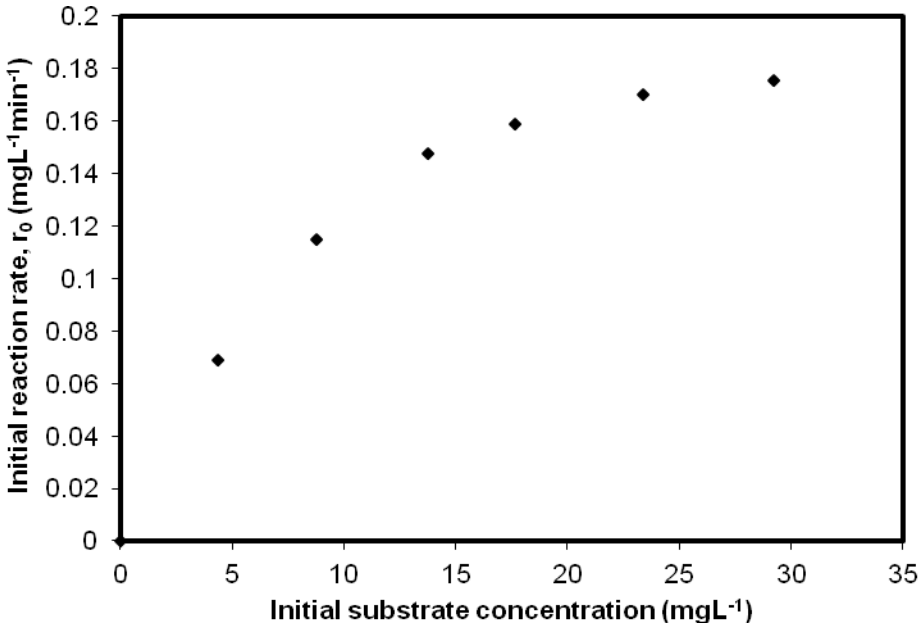


Figure 4.34: Effect of imidacloprid concentration on the initial photodegradation rate during photocatalytic degradation (TiO_2= 1.0 gL^{-1} , UV intensity = 23 Wm^{-2})

4.5.6 Effect of pH

Fig. 4.35 shows the effect of pH of the imidacloprid solution on the degradation. In this study, the pH of solution was varied from 3.5 to 9.5 with the optimum amount of catalyst 1.0 g L^{-1} at constant UV intensity of 23 W m^{-2}. The degradation increased from 80% to 95% as the pH varied from 3.5 to 6.5 and decreased thereafter. Thus, the degradation rate was slightly higher in acidic medium and decreased gradually towards basic medium (Fig. 4.8). The maximum degradation being achieved at 6.5 which was the natural pH of the imidacloprid solution.

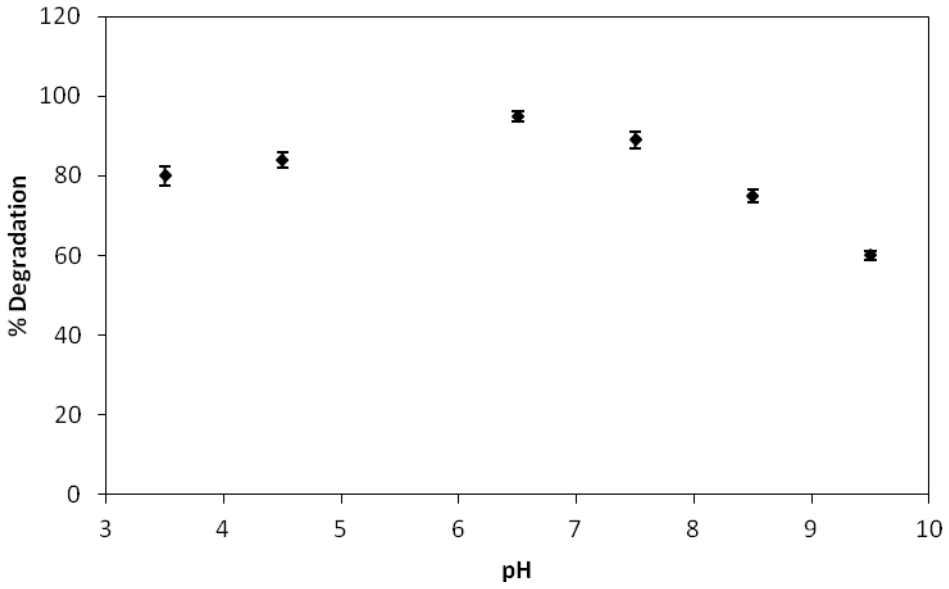


Figure 4.35: Effect of variation in pH on the photocatalytic degradation of imidacloprid (TiO_2= 1.0 gL^{-1} , H_2O_2=0.3 gL^{-1},UV intensity = 23 Wm^{-2} , C_0 = 25 mgL^{-1})

4.5.7 Effect of UV intensity

The extent of light absorption by the semiconductor catalyst at a given wavelength depends upon light intensity. The photocatalytic degradation depends primarily on intensity of UV radiations which varies throughout the year in solar conditions. For shallow pond slurry reactor, the reaction rate constant depends upon intensity as discussed in section 4.3.6. In this study, the aqueous solution of

imidacloprid with TiO_2 dose of 1.0 gL^{-1} and H_2O_2 0.3 gL^{-1} was exposed to different intensity of UV radiations keeping the A/V constant at 1.18 cm^2 mL^{-1}. As the intensity varied from 10 to 26 W m^{-2}, the degradation of imidacloprid increased from 60% to 90% (Fig. 4.36). With the increase in UV intensity, more number of OH radicals are produced as more radiations fall on the catalyst leading to high rate of degradation (Sraw et al., 2013).

For shallow pond slurry reactor, the reaction rate constant depends upon intensity as follows:

$$k/k_o = m\,[I(A/V)\,/I_o(A/V)_o]^n$$

The value of n and m thus calculated from a plot between reaction rate constant (k) and intensity of incident light, for a constant A/V ratio and the values are found to be 2.0465 and 0.0318 respectively (Fig. 4.37).

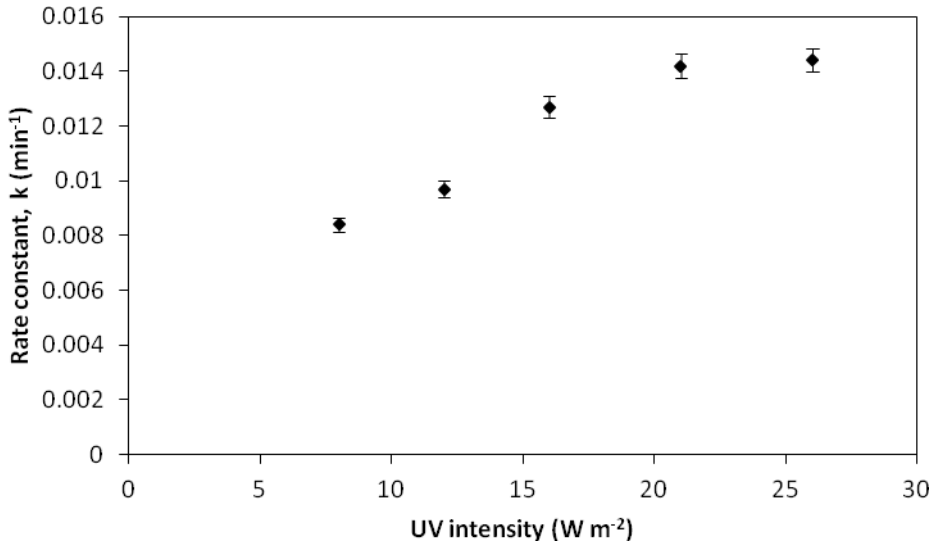


Figure 4.36: Rate constant variation with UV intensity during photocatalytic degradation of imidacloprid (TiO_2= 1.0 gL^{-1} , reaction volume = 200ml, , C_0 = 25 mgL^{-1})

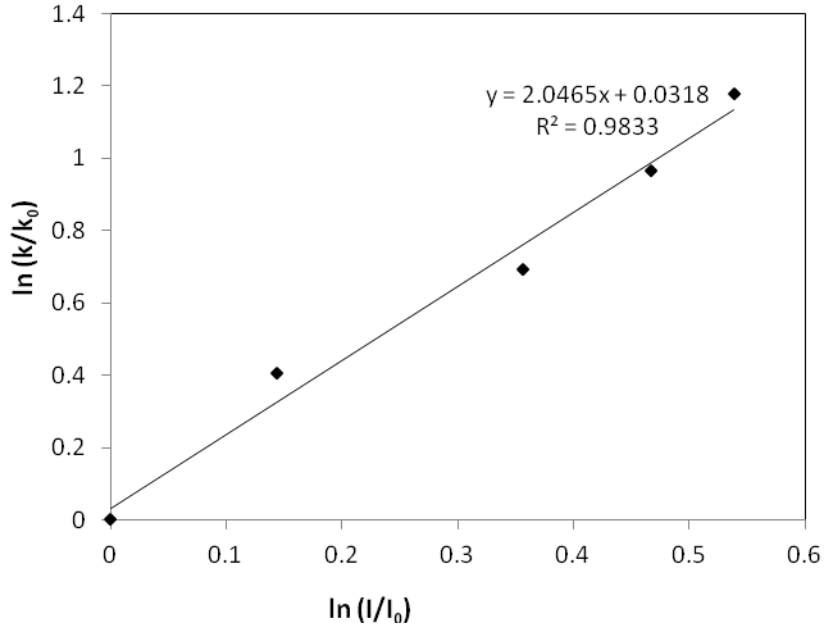


Figure 4.37: Plot of ln of rate constant vs. ln of UV intensity for the photocatalytic degradation of imidacloprid

4.5.8 Effect of area/volume (A/V)

For the photocatalytic oxidation using slurry batch reactor, depth of the reactor plays a crucial role which determines the extent of effective solar light penetration for degradation of the compound. Less depth and more area is required for more degradation, which can be achieved by either varying the area or keeping the volume constant or by keeping area constant and varying the volume. In our experiments, the area/volume (A/V) of the shallow pond reactor was varied from 0.59 to 1.77cm^2 ml^{-1}. Results confirmed the increase in the degradation efficiency with the reduction in the volume of the sample to be treated i.e. less depth (figure 4.38). With less volume keeping the area constant i.e. more A/V, more light can penetrate into the solution to be treated, leading to increase in path length of photons entering the solution resulting in higher OH radical yield with predominant electron–hole formation (Bahnemann, 2004).

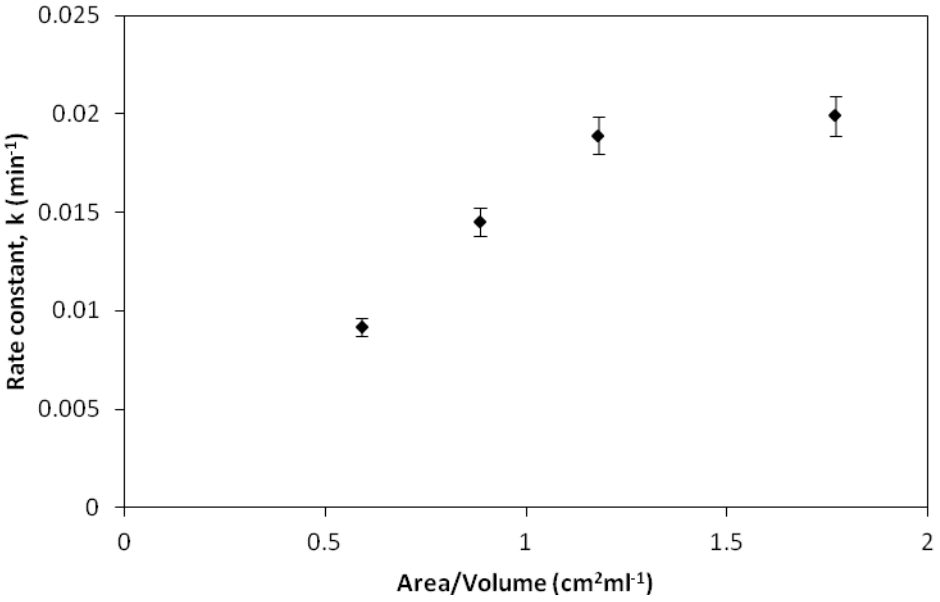


Figure 4.38: Effect of A/V ratio on photocatalytic degradation of imidacloprid (C_0= 25 mg L^{-1}, TiO_2= 1.0 gL^{-1}, H_2O_2=0.3 gL^{-1}, UV intensity = 23 Wm^{-2})

4.5.9 Catalyst recycling studies

Recycling improves the economy of any industrial process, thus role of catalyst lifetime is an important parameter for study. Especially in photocatalytic process, TiO_2 can be recycled after filtration and used in process again. Catalysts fouling due to deposition of toxic by-products and loss of the catalyst during filtration are some important points those should be looked into during recycling. For this reason, the catalyst was recycled (Fig. 4.39) after each cycle, filtered and oven dried. Results confirmed the five time recyclability of the TiO_2 with 18% reduction in efficiency. This might be due to catalyst surface fouling and loss of small amount of catalyst during filtration as discussed. With more efficient filtration system and methods to tackle fouling, photocatalytic process can become component to reduce the cost implications.

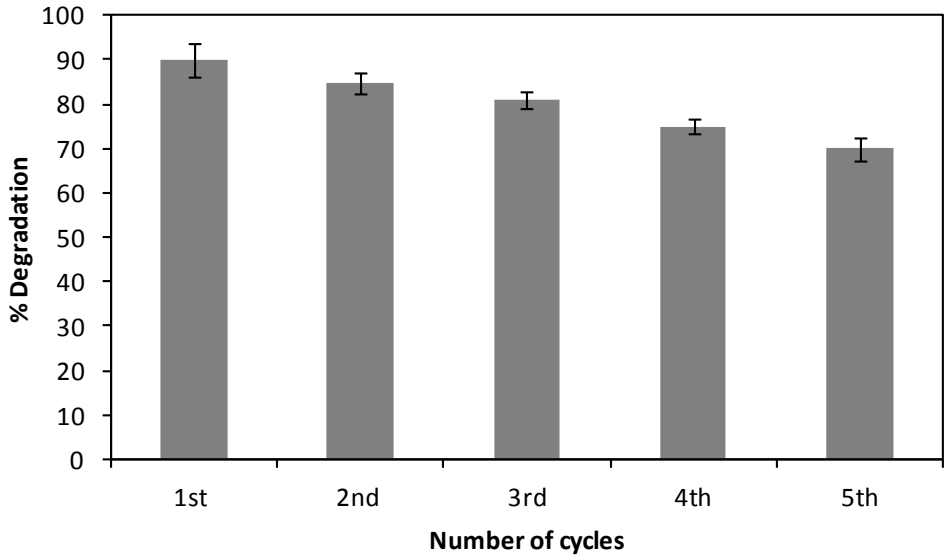


Figure 4.39: Catalyst recycling studies for the slurry mode during photocatalytic degradation of imidacloprid

4.5.10 Mineralization studies

The mineralization studies are very important for complete photodegradation of the organic compound. Generally, the pollutant degradation leads to the conversion of organic carbon into harmless gaseous CO_2 and that of hetero-atoms into inorganic ions, such as SO_4, Cl^- etc. In this study, COD reduction along with the chloride ions (Cl^{-1}) generation for studying the extent of mineralization was calculated. The maximum COD reduction of 86% was achieved after 240 min of photocatalytic irradiations experiments. Simultaneously release of Cl^{-1} ions were measured which showed 50% release during first hour of photocatalytic treatment and reached a constant value of 70% after 4 h as depicted in figure 4.40.

Hetero-atoms may compete for the active sites on the TiO_2 surface or deactivate the photocatalyst and, subsequently, decrease the degradation rate of the target molecule (Mahmoodi et al., 2007). During initial hours, the release of Cl^{-1} ions was reached maximum value owing to maximum degradation of imidacloprid. After that,

Cl^{-1} ions from solution might have competed with substrate for the active sites, leading to slow mineralization rate.

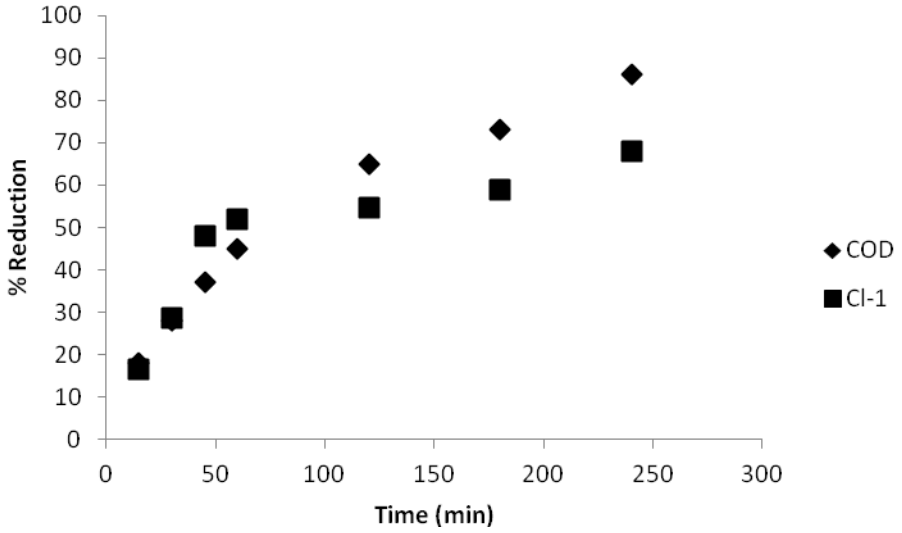


Figure 4.40: Chloride ions generation and COD reduction during the photocatalytic degradation of imidacloprid

The GC-MS analysis of the intermediate and final samples was performed to confirm about the status of intermediate products. The spectra confirmed the diminishing of parent compound along with the generation of some intermediates. The GC-MS analysis successfully detected the presence of major intermediate product as (1) Propanamide (2) Acetamide (3) Dimethyl formamide (4) Amyl nitrite and (5) 1,2-Benzene Dicarboxylic acid-3-nitro. Some of these intermediates identified for the above study have also been reported earlier (Kitsiou et al., 2009).

4.6 Photocatalytic degradation of insecticide imidacloprid using supported TiO_2: Overview

This section deals with the photocatalytic degradation of imidacloprid using TiO_2 immobilized on suitable support material, thus eliminating the cost of filtration for slurry photocatalysis. The TiO_2 immobilized cement beads described in section 3.6.2 were used to study degradation of imidacloprid. The main implication in any fixed-bed

studies is the durability of support, which in our case is checked by recycling the beads for 20-30 times. Effect of certain parameters like calcinations temperature, exposed area, UV intensity etc. are checked for studying the degradation of imidacloprid. Finally, reactor design using this support is proposed with certain modifications and is tested for degradation. An attempt has also been made to identify the intermediate products through GC-MS analysis along with the mineralization studies.

4.6.1 Preliminary Studies

Fig. 4.41 shows the reduction in concentration of imidacloprid in the presence (1.0 gL^{-1}) and absence of photocatalyst TiO_2. Simultaneously, blank experiments were performed with H_2O_2 only and using bare cement beads (without TiO_2 coating) in a batch reactor under UV/solar irradiations. In our experiments, there was no direct photodegradation (<5%) was observed and oxidant (H_2O_2) alone contributed to 7% degradation. Bare beads lead to 6% reduction in insecticide concentration owing to small adsorption characteristics of cement beads. Moreover, adsorption studies (TiO_2 P-25 only) confirmed 8% reduction in insecticide imidacloprid concentration after 5 h of irradiations. Thus, the observed degradation of imidacloprid is particularly due to the photoactivation of semiconductor oxides i.e. photocatalysis. The loss in imidacloprid concentration in presence of catalyst only owes to adsorption of compound on TiO_2 P-25, is mainly due to the formation of monolayer of the imidacloprid on the catalyst surface. No free active sites would be available after the monolayer formation, and therefore no further reduction in concentration was observed (Toor et al., 2007). As a result, photolytic and adsorption was not considered to be significant contributors for imidacloprid removal in the subsequent experiments. However, UV + H_2O_2 + TiO_2 coated beads showed 89% degradation after 6 h of illumination, thus leading to an assumption that adsorption-desorption of the imidacloprid and reaction intermediates

are relatively slow as compared to the formation of electron/hole pairs (Haque and Muneer, 2003). Slurry photocatalysis for the degradation of imidacloprid is, no doubt, more effective (94% degradation in 3h), however the catalyst separation from slurry is not feasible.

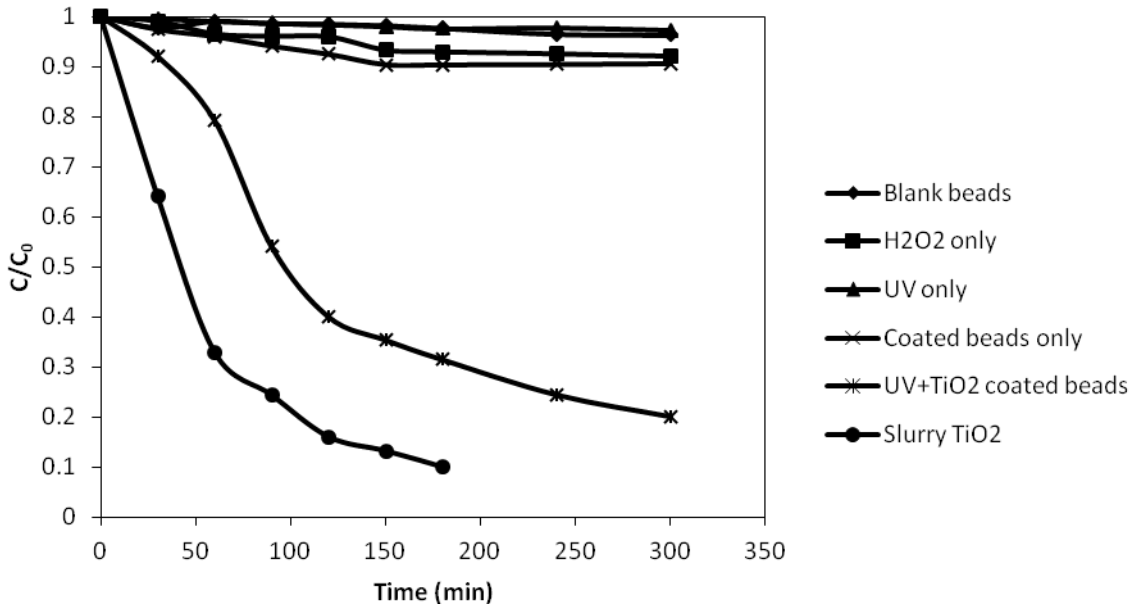


Figure 4.41: Photolysis, photocatalytic reduction of imidacloprid in the presence and absence of TiO_2 along with adsorption and slurry TiO_2 studies. Experimental conditions: C_0= 25 mgL^{-1}, V= 200 ml, UV intensity = 23 Wm^{-2}

4.6.2 Effect of number of TiO_2 coatings on cement beads

As discussed in section 4.4.2, the stability and thickness of the TiO_2 layer on the immobilized surface both are very important for its continuous use for the degradation of pesticides. Similar studies have been performed in this section to study the effect of TiO_2 coatings on the immobilized surface for the photocatalytic degradation of imidacloprid. The thickness of TiO_2 on the support material was varied with each cycle of coating (as mentioned in section 3.6.2). The thickness of the film was increased with each level of coating on cement bead depending upon its size and texture. The degradation of imidacloprid was 55% with one cycle of coating and reached to a

stabilized value of 89% after 6 h of photocatalytic treatment as number of coatings increased from 2 to 4 (Fig. 4.42). With each cycle of TiO_2 coating on cement bead, although thickness of the film increases but, the catalyst particles were loosely bound and were susceptible to detachment from the immobilized surface. They were not firmly bound to the surface and therefore the degradation data became constant after second coating, which was optimal value in this case. Moreover, it was not an economical approach to have more coatings of TiO_2 without actually increase in degradation.

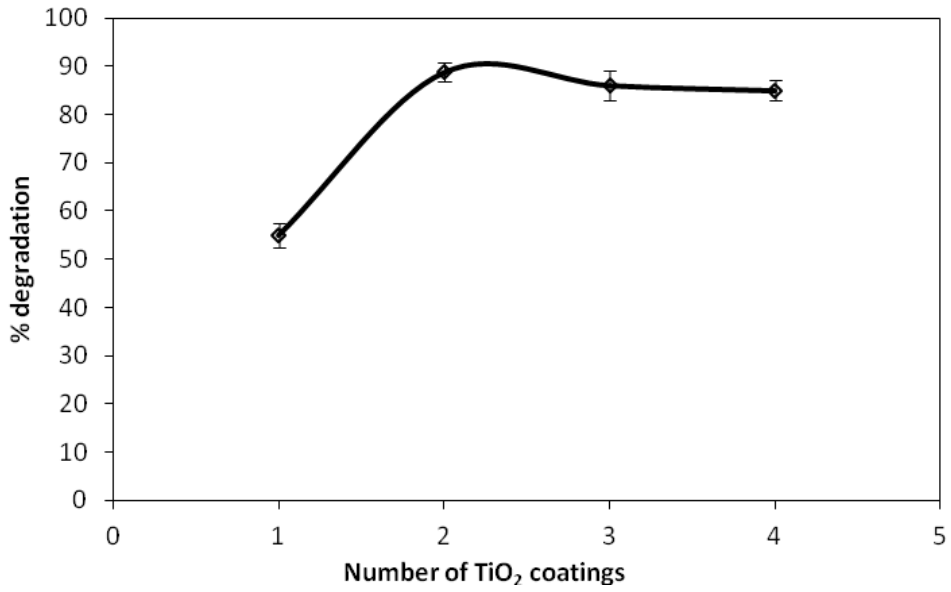


Figure 4.42: Effect of number of TiO_2 coatings on cement beads for photocatalytic reduction of imidacloprid. Experimental conditions: C_0= 25 mgL^{-1}, V= 200 ml, UV intensity = 23 Wm^{-2}

4.6.3 Effect of calcination temperature

In immobilization studies, the stability of catalyst layer on support depends upon how the curing of the support is being carried out with temperature. Heat treatment influences the specific surface of the photocatalyst along with affect on the surface defects and active sites (Anderson and Bard, 1997; Shifu and Gengyu, 2005).

If the curing of the layer on the support is not effective in terms of heat treatment, the catalyst particles will lose their hold from the surface and thus will detach. In our experiments, the TiO_2 coating on the cement beads was cured by calcining the beads at different temperatures i.e. 200, 300 and 400 ^oC for 2 h. The photocatalytic activity of beads calcined at different temperatures was determined by degradation efficiency of imidacloprid. The maximum degradation efficiency achieved was 89±6.5% when the beads are calcined at 400 ^oC and lower temperatures didn't contribute effective results (i.e. < 71%). At higher temperatures, the stability of the coating was also a point of concern, as increase in calcination temperature beyond 400 ^oC did not enhance the degradation rate.

4.6.4 Durability studies

The durability of the immobilized TiO_2 catalyst on cement beads was well documented in section 4.2.7, where beads were recycled for atleast thirty cycles for the degradation of IPU. Similarly, in this study, TiO_2 coated cement beads were effectively recycled for at-least twenty times with 20% reduction in efficiency in context to degradation of imidacloprid as shown in figure 4.43. The reduction in efficiency of the supported system might be due to accumulation of intermediates by-products in the cavities or on the surface of the support thus blocking the sites for adsorption, which reduces the catalytic activity.

The calcination or heat treatment of the used beads was necessary in order to maintain the activity of catalyst. In this view, coated cement beads were subjected to heat treatment at 100 ^oC for one hour for reactivation. During first five to ten cycles, the rate of degradation was restored and it was equivalent to fresh coated beads. After tenth cycle, the activity was reduced, might be due to over deposition of degradation by-products. From SEM images and EDAX analysis, it is clear that catalyst is intact

even after 20th recycle confirming its stability, hence can also be further used as such. The actual images of coated cement beads during various stages of recycling are shown in Fig. 4.24 (section 4.2.7).

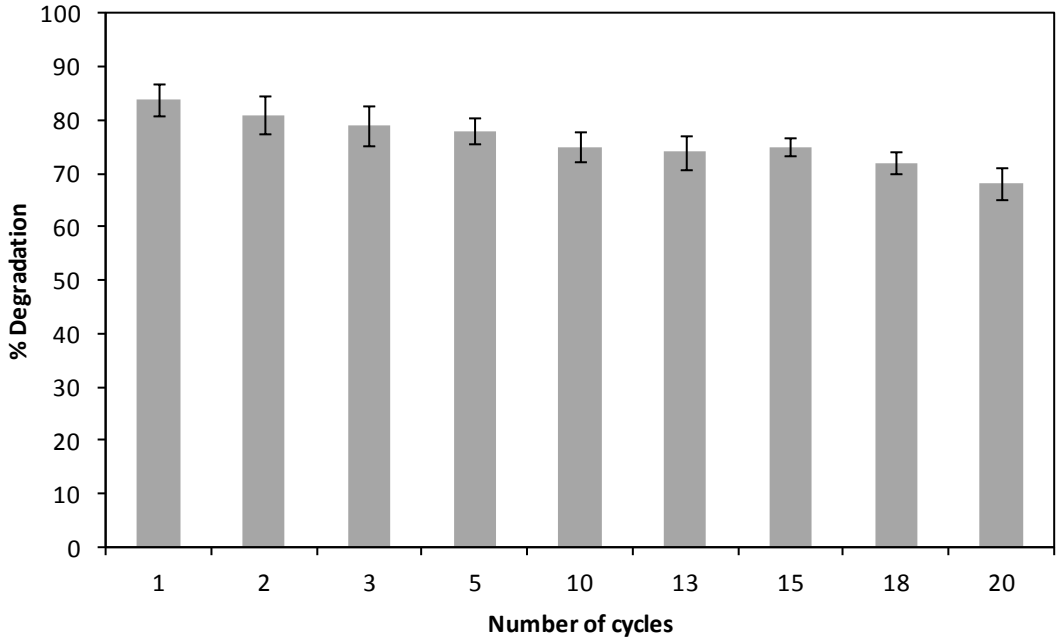


Figure 4.43: Recycling of TiO_2 coated cement beads for photocatalytic reduction of imidacloprid. Experimental conditions: C_0= 25 mgL^{-1}, V= 200 ml, UV intensity = 23 Wm^{-2}

4.7 Scale-up studies for slurry and fixed-bed photocatalytic reactors for the degradation of pesticides

4.7.1 Overview

In order to promote the feasibility of photocatalytic water treatment technology at industrial scale in near future, scale-up trails of lab results are mandatory. In our studies, lab-scale studies discussed in sections 4.3, 4.4, 4.5 and 4.6 proved to be successful for the degradation of selected pesticides both in slurry and fixed form. Industrial applications of these results would be visualized, if proto-type reactors were successful in degrading the studied pesticides. In this context, scale-up trails have been performed for implementing the lab scale results.

Both slurry reactor as well as re-circulating fixed-bed type pilot-scale reactor has been designed and used for the degradation of pesticides. In slurry reactor, the study of various parameters has been done like depth of solution to be treated, flow-rate variation for constant area/volume. The catalyst dose optimized for batch slurry reactor has been selected and accordingly used for scale-up studies. The catalyst recycling studies have been tried to our best in case of pilot-scale slurry reactor.

The parabolic trough concentrator (PTC) has been used for the degradation of pesticide solution using immobilized TiO_2 catalyst (cement beads) under concentrated sunlight. TiO_2 coated cement beads used in batch studies have been tested for their durability in pilot-scale fixed-bed reactor in recirculation mode. Effect of flow rate of pesticide solution on the degradation has been studied using solar irradiations. In general, the efficacy of fixed-bed photocatalysis in degrading pesticides opens up channels for commercial applications of this technology for in-situ pesticide treatment.

4.7.2 Photocatalytic degradation of herbicide IPU using pilot-scale slurry reactor

Scale-up studies have been performed using slurry batch reactor for the photocatalytic degradation of herbicide isoproturon with working volume of 6 L. The catalyst dose used for scale-up studies was equivalent to dose optimized at lab-scale slurry batch reactor i.e. 0.5 gL^{-1} with initial herbicide concentration of 25 mgL^{-1} at 5.2 pH. Slurry batch reactor used for scale-up studies was made of galvanised iron sheet with cement base with average diameter of 50 cm and 18 cm depth (Fig. 4.44). Aerator was attached to the tubes used to provide the aeration in the slurry reactor. The flow rate and pressure of bubbled air was maintained enough to create turbulence in the slurry. The purpose of turbulence was to enhance the mass transfer between photocatalyst and target pollutant in the presence of light. Turbulence also prevented the settling of the catalyst; keeps it in suspension, thus enhancing the degradation rate. In present studies, pilot-scale slurry batch reactor was operated for 4.5-5.0 h for the degradation of herbicide IPU and 85 ± 2% degradation was achieved under solar irradiations as shown in figure 4.45, whereas blank run (without TiO_2) gave only 7% degradation. The average UV solar intensity was 25 ± 5 Wm^{-2} during the experimental days.

Although the slurry batch reactors are easy to design/fabricate and operate, the catalyst separation from the slurry always a hurdle for their practical applications. Moreover, these reactors are of non-concentrating types, effective sunlight exposure throughout the day is not effective. Land requirements are also large for these types of reactors, which is not economically viable option (Marugan et al., 2008; Marugan et al., 2009).

Figure 4.44: Pilot-scale slurry batch reactor

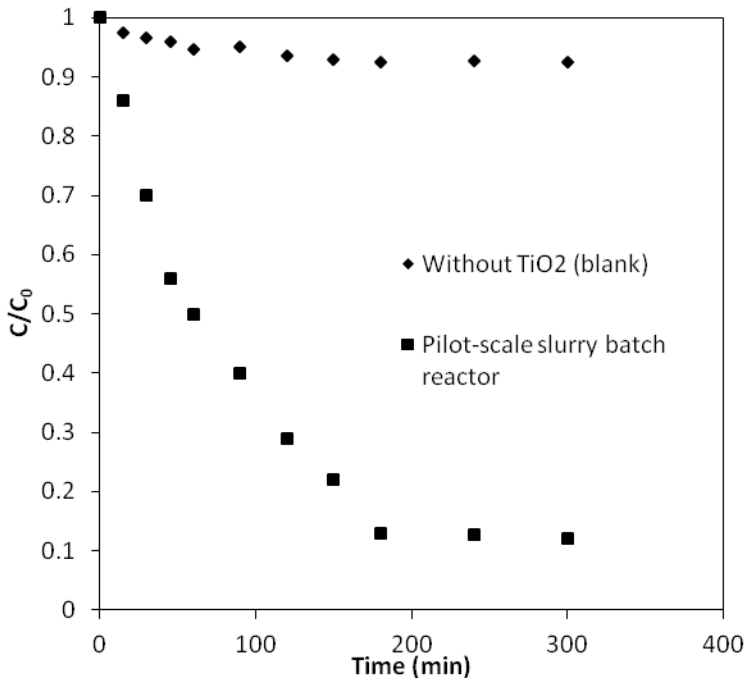


Figure 4.45: Concentration variation for the degradation of herbicide IPU using pilot-scale shallow slurry batch reactor (C_0 = 25 mgL^{-1}, pH = 5.2)

4.7.2.1 Effect of area/volume (A/V)

For shallow pond reactors, the area available for irradiation of solar light is very important. The photocatalytic process in these reactors depends primarily on the area available for irradiations and depth up to which the rays can penetrate. Thus, area to volume (A/V) of the reactor is very important factor when practical applications of slurry photocatalytic process are to be decided. Generally, the degradation increases with increasing aperture to volume ratio of shallow pond slurry reactor. As A/V ratio is increased from 0.2804 to 0.9815 cm^2 mL^{-1}, the degradation increased from 71% to 91% in almost 4.5 h with initial IPU concentration of 25 mgL^{-1} as shown in figure 4.46.

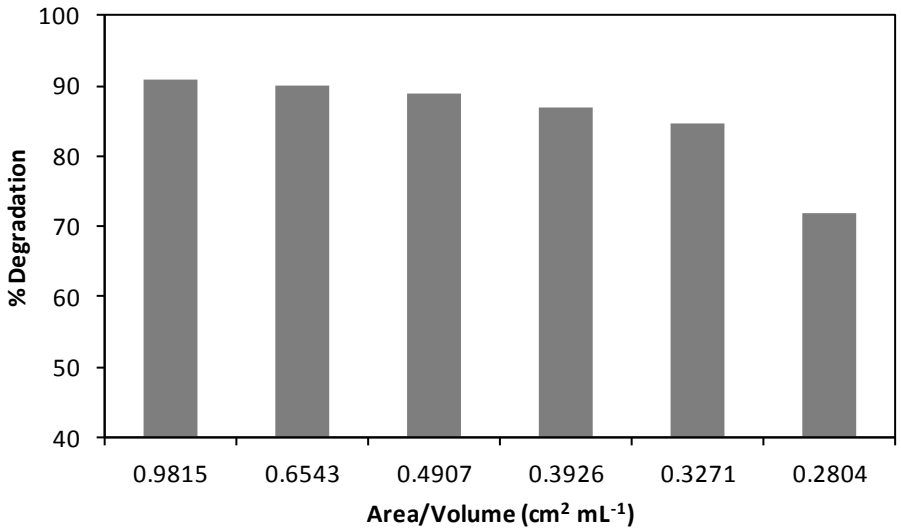


Figure 4.46: Effect of A/V on the degradation of herbicide IPU using pilot-scale shallow slurry batch reactor (C_0 = 25 mgL^{-1}, pH = 5.2)

Surface area can be increased by either increasing the aperture and keeping the volume constant or by keeping the aperture constant and varying the volume. In this case, the volume has been varied by keeping the aperture constant i.e. depth of the solution was varied. With certain design modifications and operating conditions, reactor could be used for field-scale applications as pre/post treatment options.

4.7.2.2 Comparison between lab and pilot-scale slurry reactors

Lab-scale studies using slurry batch reactor (volume 200 mL) with A/V ratio 1.18 cm^2 mL^{-1} yielded more than 90% degradation of IPU at optimum conditions after 3.5-4.0 h. Scale-up studies confirmed 85% degradation of IPU after 4.5-5.0 h of photocatalytic treatment with total working volume of 6 L (Fig. 4.47) and A/V ratio 0.9815 cm^2 mL^{-1}. Thus, pilot-scale photocatalytic studies have shown the potential for degrading the pesticides with optimized conditions at lab-scale. Mass transfer limitations along with low photonic efficiency might be some constraints for pilot-scale and thus industrial scale. These limitations can be overcome by better methods for aeration, which further increase the gas-liquid contact, thereby reduce the mass transfer limitations. Photonic efficiency can be improved by varying the design of reactor for solar photocatalytic treatment. Rectangular slurry reactors with sufficient depth would be designed to capture maximum surface area to volume ratio. This would allow achieving maximum photonic efficiency, leading to higher degradation rates.

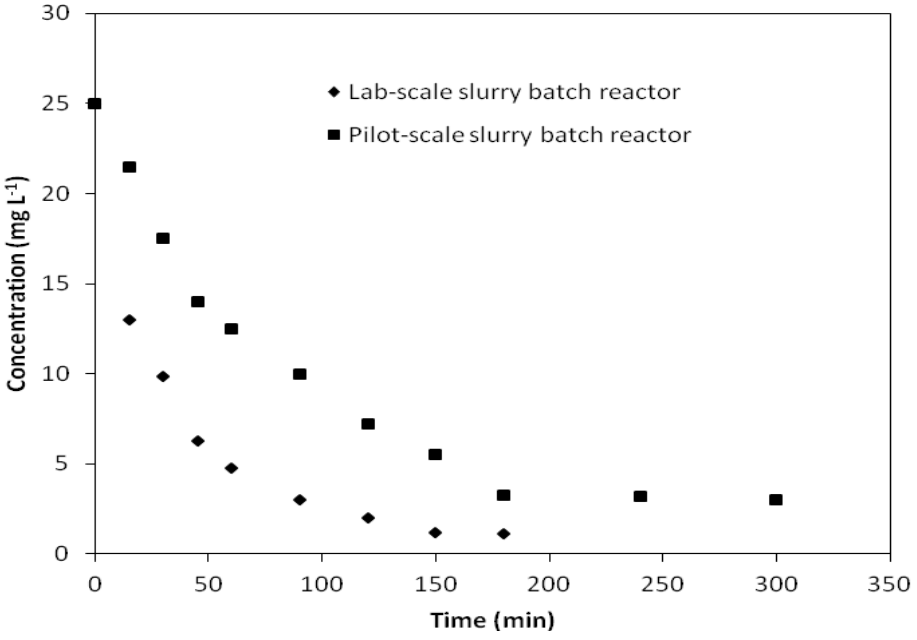


Figure 4.47: Performance comparison between lab-scale (volume 200 mL) and pilot-scale (volume 6 L) batch slurry reactors for the degradation of herbicide IPU (C_0 = 25 mgL^{-1}, pH = 5.2)

One of major drawback for large-scale solar photocatalytic applications is that surface area required would be very large. Such surface areas can be reduced significantly if photocatalysts are modified to have an increased surface reaction efficiency and electron-hole trapping efficiency (Motegh, 2014).

4.7.3 Fixed-bed pilot-scale reactor for photocatalytic degradation of herbicide IPU

A pilot-scale re-circulating type fixed-bed reactor was employed for the photocatalytic degradation of herbicide IPU. The efficacy of supported TiO_2 catalyst on cement bead was checked for IPU degradation and durability was checked by recycling the used beads. The effect of flow rate of herbicide solution on degradation was studied.

A solar parabolic concentrator (PTC) was used for studying the degradation of IPU using TiO_2 coated cement beads. The details of PTC used in this study are discussed in section 3.6. The receiver tube in PTC was packed with sufficient number of coated TiO_2 cement beads. The herbicide IPU solution (C_0 = 25 mL^{-1}) at optimized pH 5.2 was made to circulate through the reactor with flow rate of 1 L min^{-1}. The reactor treated 6.0 L of herbicide solution in a re-circulation mode. Temperature sensors were used to measure the temperature of the circulating solution. The temperature range was found to be between 50 and 100^0C depending upon position of collector and time of the day. Although the temperature increases by decreasing the diameter of the receiver tube as decrease in diameter reduces the surface area which results in energy losses (Malato, 2002; Reddy and Ravikumar, 2012). However, to increase the degradation rate of herbicide IPU, large surface area is required to ensure (i) maximum solar radiation penetration through the transparent receiver tube and (ii) large number of cement balls could be accommodated in the tube. The receiver

diameter was kept 2.54 cm to get required temperature and relatively large area. UV intensity was also measured by radiometer throughout the experimental time i.e. between 10.00 a.m. to 2.30 p.m. Samples were taken at regular intervals of 30 min and analyzed for degradation.

Figure 4.48 shows pictorial representation of PTC at different angle of inclinations throughout the day. The retention time of IPU solution was found to be 90 s depending upon flow rate. The herbicide IPU degradation observed was 20% and 91% after 4 h under concentrated solar irradiation without TiO_2 (blank) and with immobilized TiO_2 respectively as shown in figure 4.49.

Figure 4.48: Representation of Solar Parabolic Collector at the angle of inclination of (a) -40^0 (b) 0^0 (c) 20^0 (d) 40^0 respectively.

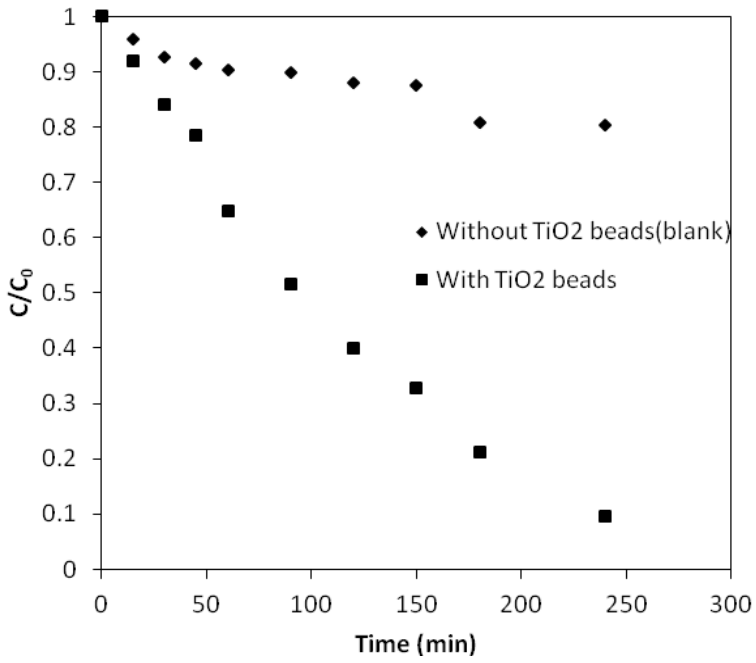


Figure 4.49: Degradation of IPU with and without TiO_2 coated cement bedas using pilot-scale fixed-bed photoreactor, PTC (C_0 = 25 mgL^{-1}, Total volume = 6 L)

The parabolic collector concentrates the UV radiations at the focal line containing immobilized beads leading to high UV intensity which leads to production of more hydroxyl radicals (Arasu and Somakumar, 2007). Thus, with some design modification, optimizing the operating conditions the PTCs can be promising tools for the treatment of bio recalcitrant compounds for its commercial applications.

4.7.3.1 Effect of flow rate

With re-circulating type flow reactors, the flow rate of solution to be treated is very important parameter. Especially in fixed-bed photocatalytic reactor, along with affecting the degradation, the flow rate also affects weathering of catalyst from the surface. In our studies, we have studied the three different flow rates using PTC i.e. 0.5 $Lmin^{-1}$, 1.0 $Lmin^{-1}$ and 2.0 $Lmin^{-1}$ of herbicide IPU and effect on the degradation was observed. The degradation observed was 70, 92 and 78 % at flow rates of 0.5 $Lmin^{-1}$, 1.0 $Lmin^{-1}$ and 2.0 $Lmin^{-1}$ respectively for the photocatalytic treatment using PTC (Fig.

4.50). As the flow rate was increased beyond 1.0 $Lmin^{-1}$, the degradation efficiency decreased. With increased flow rates, the retention time was reduced, thus solution would be exposed for lesser time during exposed area. Deceasing the flow rate would lead to increase in the treatment time of target pollutant, which is not recommended economically. Thus, residence time play an important role in determining the efficacy of the process.

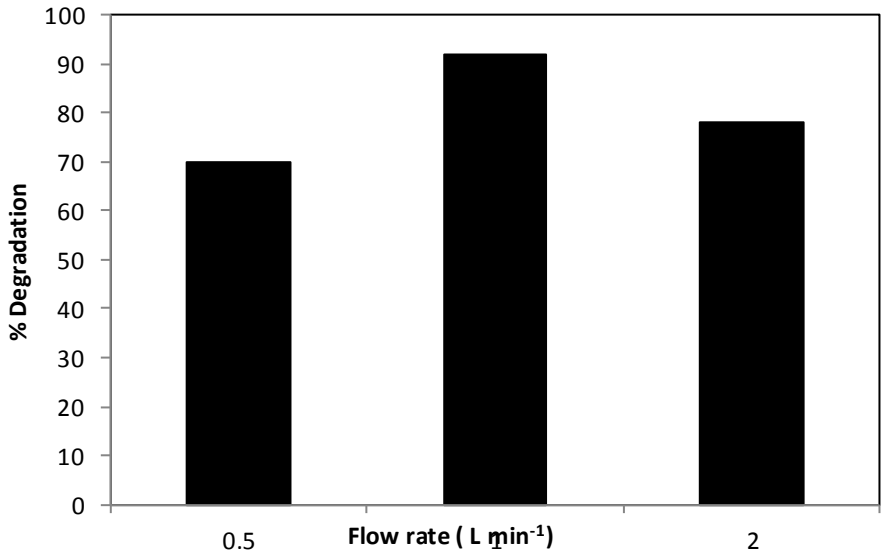


Figure 4.50: Effect of flow rate of IPU on the photodegradation using fixed-bed photoreactor, PTC (C_0 = 25 mgL^{-1}, Total volume = 6 L)

4.7.3.2 Recycling studies

The durability of the supported catalyst activity was also investigated in terms of photocatalytic degradation of IPU using PTC. For flow conditions, the catalyst stability on support material is always a big concern. If the catalyst layer is not firmly attached to the surface, it is most susceptible to detach from surface with flow variations. In our experiments, it was found that after seven to eight runs using the same batch of TiO_2 immobilized beads, the catalyst activity was not significantly affected as compared to fresh batch (Fig. 4.51). There was 10-15% reduction in degradation efficiency of herbicide IPU.

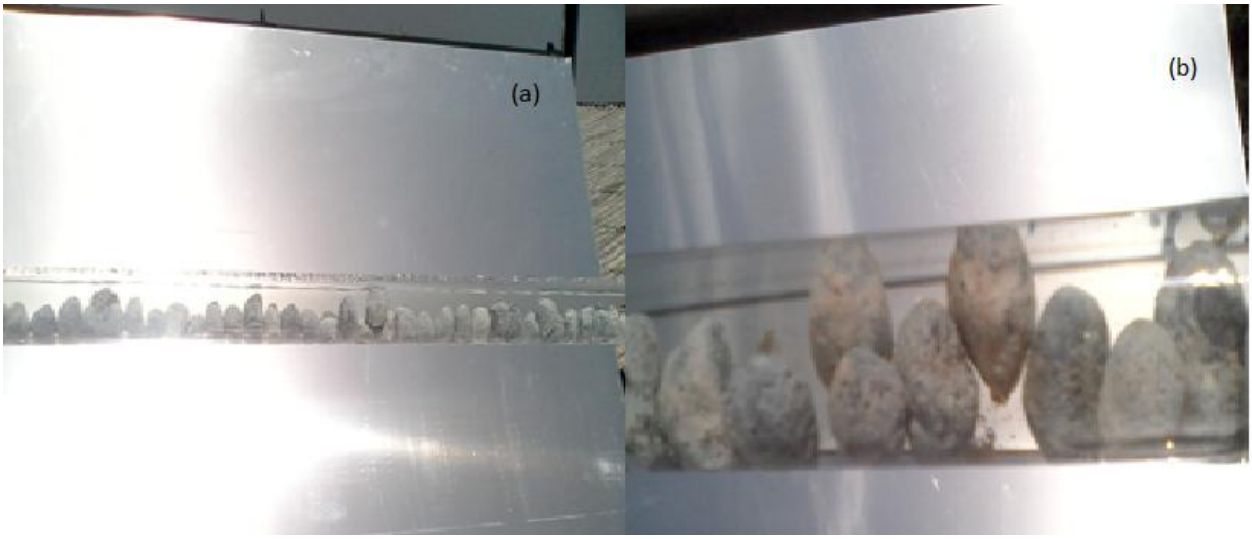


Figure 4.51: Pictorial representation of TiO_2 immobilized cement beads (a) fresh batch and (b) after eighth cycle.

The loss in activity of the coated beads could be either due to loss of catalyst from the surface due to continuous flow conditions or due to blocking of catalytic active sites of TiO_2. The loss of catalytic activity due to site blocking could be recovered by heating the beads at higher temperature. Better immobilizing techniques could be tried for fixing the catalyst, so that weathering of coated beads could be minimized.

4.7.3.3 Comparison between lab and pilot-scale fixed-bed reactors

Lab-scale studies using TiO_2 immobilized cement beads yielded 95% degradation after 4 h of photocatalytic treatment under optimized conditions as discussed in section 4.4 with operating volume of 200-300 mL. Scale-up studies for fixed-bed reactor (PTC) as discussed above gave 91% degradation of IPU in 4 h with 6 L working volume. Little reduction in efficiency might be due weathering of immobilized TiO_2 from the surface due to continuous flow conditions. However, the pilot-scale fixed-bed reactor proved to be efficient in treated pesticide contaminated water with working volume of 6 L (Fig. 4.52). These concentrated type reactors have

advantage of concentrating solar radiations at the axis packed with coated beads, thus leading to increase in intensity and working temperature. Both these factors lead to effective degradation of IPU in this case with more volume under study as compared to lab-scale reactors.

With certain modifications in design of fixed-bed pilot-scale reactors along with operating conditions, more volume can be treated effectively in less amount of time. Results from pilot studies give way for the field-scale applications for in-situ remediation of pesticides from groundwater.

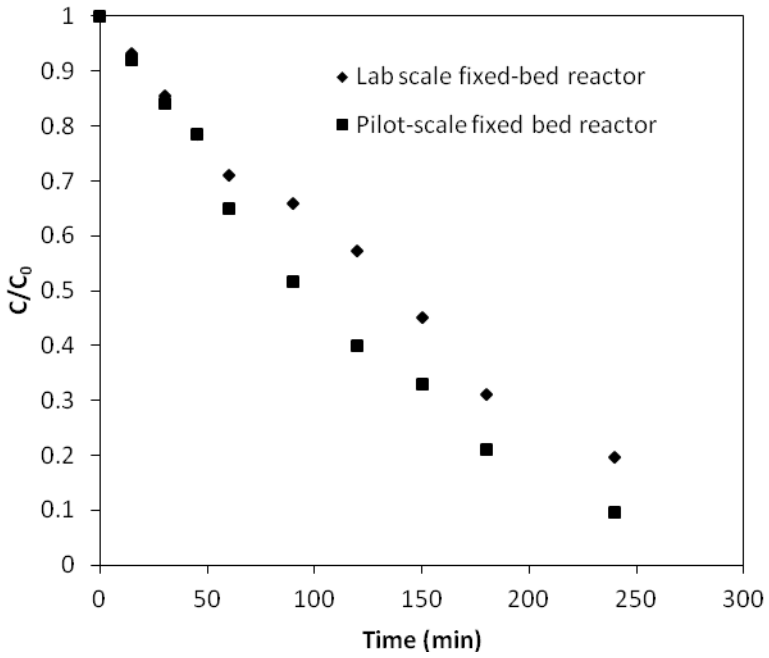


Figure 4.52: Performance comparison between lab-scale (volume 200-300 mL) and pilot-scale (volume 6 L) fixed-bed reactors for the degradation of herbicide IPU (C_0 = 25 mgL^{-1}, pH = 5.2)

4.7.4 Performance comparison between pilot-scale slurry and pilot-scale fixed bed reactor

For industrial scale applications, viability of results as well as success of pilot-scale reactor is a major concern. For AOPs, the catalyst can be in suspended form or in fixed form as discussed. The outcome of the study at pilot-scale proposes the effectiveness of individual photocatalytic treatment for degradation of pesticides like

IPU present in water/wastewater. The degradation of IPU achieved was 85 ± 2% with pilot-scale slurry batch reactor operated for 4.5-5.0 h and correspondingly 91% degradation was observed after 4 h under concentrated solar irradiation with immobilized TiO_2 using PTC. Although overall degradation was slightly higher in case of PTC, but degradation was faster in case of slurry reactor as shown in figure 4.53. There is no mass transfer limitations in case of slurry reactors due to turbulence, thus pollutants have easy access for the catalyst's active sites, leading to faster degradation rates. Slurry photocatalysis using TiO_2 can be implemented as pre or post treatment for degrading pesticides where conventional treatments are not effective for removing these types of contaminants. For handling large volumes of wastewater in industry, slurry pond reactors can be installed, as there are no size limitations. Their fabrication cost is low or even the biological ponds in the industry can be used as slurry reactors.

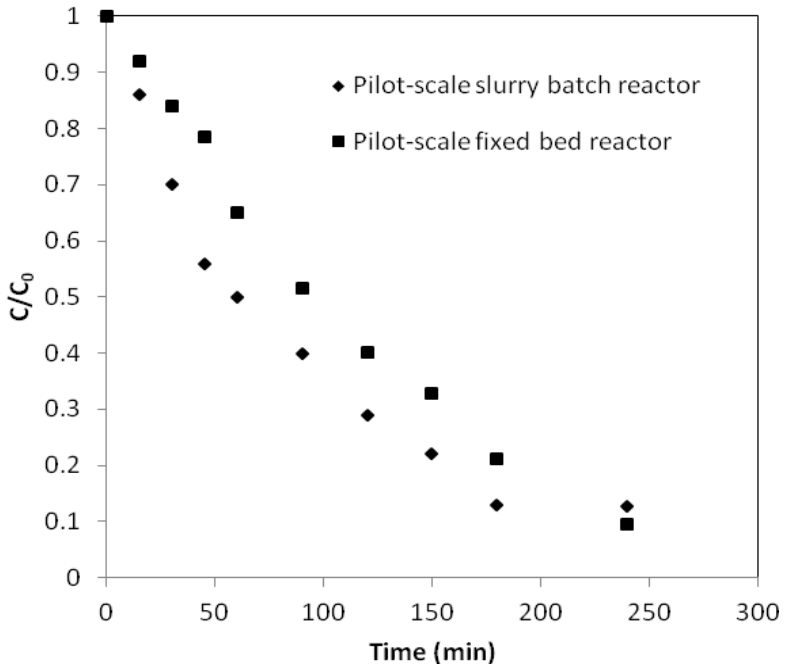


Figure 4.53: Performance comparison pilot-scale slurry and pilot-scale fixed bed reactor for the degradation of herbicide IPU (C_0 = 25 mgL^{-1}, pH = 5.2)

These slurry photocatalytic reactors can be used as pre or post polishing step to the biological treatment process. However, site test with proto-type system should be conducted with all design kinetics prior to developing the industrial scale slurry pond reactor.

For fixed-bed reactors, they have demonstrated a great potential for the applications of AOP as a pre-treatment method that can be followed by a biological treatment in degrading bio-recalcitrant compounds like pesticides. However, there are certain factors which can be looked into for more successful applications of fixed-bed catalysis like low manufacturing installation, easy operation, maximum solar coverage and low maintenance costs. For easy handling, multiple reactors (low volume) can be operated in series in continuous mode and number of such units would be modelled out using reactor kinetics.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study presented the heterogeneous photocatalytic degradation and mineralization of isoproturon and imidacloprid using TiO_2 in slurry mode as well immobilized form. The oxidation proceeds with first-order kinetics and the photocatalytic reaction rate strongly depends on parameters like photocatalyst concentration, initial substrate concentration, pH, UV intensity for slurry case and number of coatings, size of bead, temperature for fixed-bed catalysis, thus deciding the optimized conditions.

The optimized parameters for the degradation of IPU are TiO_2 loading 0.5 g L^{-1}, pH 5.0, C_0=25 mg L^{-1} in case of lab-scale slurry mode reactor (section 4.3). The subsequent reduction in COD (96%) and TOC (90%) along with ammonium ion generation confirmed the mineralization of the herbicide, IPU through various intermediate compounds as evident through HPLC and LC-MS data. A suitable pathway was suggested from the intermediates (degradation products) through LC-MS analysis.

The heterogeneous photocatalytic degradation and mineralization studies have been attempted for the degradation of insecticide imidacloprid (section 4.5). The effect of various parameters for process optimization has been studied like catalyst dose, oxidant addition, UV intensity, area/volume etc. For the existing conditions, TiO_2 loading 1.0 g L^{-1}, H_2O_2 3.0 g L^{-1} at 26 W m^{-2} UV intensity is the optimized values for obtaining the better degradation rates. The 86% reduction in COD value along with

chloride ion generation confirmed the mineralization of insecticide. The intermediates study has also been performed using GC-MS to confirm the by-products and their subsequent degradation. The outcome of the study proposes the effectiveness of the photocatalytic treatment for degradation of pesticides like IPU and imidacloprid present in water/wastewater. Slurry photocatalysis using TiO_2 can be implemented as pre or post treatment for degrading insecticides where conventional treatments are not effective for removing these types of contaminants. For handling large volumes of wastewater in industry, slurry pond reactors can be installed, as there are no size limitations. Their fabrication cost is low or even the biological ponds in the industry can be used as slurry reactors. These slurry photocatalytic reactors can be used as pre or post polishing step to the biological treatment process. However, site test with proto-type system should be conducted with all design kinetics prior to developing the industrial scale slurry pond reactor.

Although effective, slurry mode often presents problems in terms of catalyst separation, thus needs complex filtration procedure and the high turbidity decreases the radiation flux. Drawbacks of slurry mode photocatalysis can be eliminated by immobilizing the catalyst on suitable support material using glass sheet, small cement slabs and cement beads. The study in section 4.4 and 4.6 shows use of immobilized TiO_2 on cement beads for the degradation of herbicide IPU and insecticide imidacloprid respectively. The effect of bead diameter as well as number of coatings has been studied for the first time along with its durability studies. The parameters like UV intensity, oxidant concentration (H_2O_2), effect of calcination temperature play important role affecting the photocatalytic degradation rate, thus deciding the optimized conditions. Two coatings of TiO_2 on cement beads of 1.5 cm diameter calcined at 400 ^oC proved best optimum conditions for the degradation of IPU and imidacloprid. The

COD reduction (92%) along with ammonium ion generation (80%) confirmed the mineralization of the herbicide, IPU and COD reduction (86%) with 70 % chloride (Cl^-) ion generation confirmed the mineralization of imidacloprid. From SEM and EDAX analysis, catalyst stability is proved even after 30^{th} recycle, thus confirms its applications for several cycles for the degradation of pesticides without losing its original activity.

The investigation in section 4.7 demonstrates successful use of pilot-scale reactors slurry as well as fixed-bed reactors for the degradation of pesticides. In case of fixed-bed, parabolic trough collector (PTC) was employed for the degradation of IPU using cement beads coated with TiO_2. The degradation efficiency achieved was 91% with IPU flow rate optimized at 1.0 L min^{-1} with total working volume of 6 L.

Scale-up studies have also been performed using slurry batch reactor for the photocatalytic degradation of herbicide isoproturon with working volume of 6 L. The degradation of herbicide IPU was 84% under solar irradiations with average UV solar intensity of 25 ± 5 Wm^{-2}.

Working and execution of pilot-scale reactors is very fruitful to extend these results for a technology development with the present leads.

5.2 Recommendations

Photocatalytic technologies (AOP) have shown their potential for treating the water/wastewater containing biorecalcitrant compounds like pesticides. However, the operating cost for AOP is always higher than conventional treatment technologies. Thus future research would aim towards the cost reduction in terms of efficient catalysts, use of solar spectrum etc. for practical applications of AOP.

The possibility of coupling AOP (pre or post treatment) with conventional biological systems for the treatment of pesticides can be worked out, where individual

technology may not be sufficiently effective. Better kinetic models would help in finding the right direction in research and development of solar photocatalysis.

Future research must also investigate the effectiveness of more efficient pilot-scale reactors. Better retention time, area exposed, durability and techno-economic analysis are certain components, which certainly improve the commercial viability of solar photocatalytic technology.

REFERENCES

1. Aharonson N., Cohen S. Z., Drescher N., Gish T. J., Gorbach S., Kearney P. C., Otto S., Roberts T. R. and Vonk J. W., Potential contamination of ground water by pesticides, *Pure and Applied Chemistry***,** 59 (1987) 1419–1446.
2. Alexiadis A. and Mazzarino I., Design guidelines for fixed-bed photocatalytic reactors, *Chemical Engineering and Processing*, 44 (2005) 453–459.
3. Álvarez P.M., Beltrán F.J., Jaramillo J., Pocostales P. and Márquez G., Comparison of various advanced treatment methods for municipal wastewater reclamation. *World Academy of Science, Engineering and Technology*, 5 (2011) 561-562.
4. Amorisco A., Losito I., Palmesano F. and Zambonin, P. G., Photocatalytic degradation of the herbicide isoproturon: Characterisation of by-products by liquid chromatography with electrospray ionisation tandem mass spectrometry, *Rapid Communications in Mass Spectrometry*, 19 (2005) 1507–1516.
5. Anderson. C., Bard A. J., 1997. Improved photocatalytic activity and characterization of mixed TiO_2/SiO_2 and TiO_2/Al_2O_3 materials, *Journal of Physical Chemistry: B*, 101 (1997) 2611-2616.
6. Andreozzi R., Caprio V., Insola A., Longo G. and Tufano V., Photocatalytic oxidation of 4-nitrophenol in aqueous TiO_2 slurries: An experimental validation of literature kinetic models, *Journal of Chemical Technology and Biotechnology*, 75 (2000) 131-136.
7. Anpo M., Use of visible light. Second-generation TiO2 photocatalysts prepared by the application of an advanced metal ion-implantation method, *Pure and Applied Chemistry*, 72 (2000) 1787-1792.

8. APHA, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, 18th ed., Washington DC, 1992.

9. Arasu V. and Sornakumar T., Design, manufacture and testing of fiberglass reinforced parabola trough for parabolic trough solar collectors, *Solar Energy*, 81 (2007) 1273–1279.

10. Areerachakul N. and S. V., Granular activated carbon (GAC) adsorption-photocatalysis hybrid system in the removal of herbicide from water, *Separation and Purification Technology*, 55 (2007) 206-211.

11. Arias E. M., López P. E., Simal G. J., Mejuto J. C. and García R. L., The mobility and degradation of pesticides in soils and the pollution of groundwater resources, *Agriculture, Ecosystems and Environment***,** 123 (2008) 247-260.

12. Arslan İ., Balcıoğlu A. I. and Bahnemann D. W., Advanced chemical oxidation of reactive dyestuffs in simulated dyehouse effluents by the ferrioxalate-fenton/UV-A processes, *Dyes and Pigments*, 47 (2000) 207-218.

13. Augugliaro V., Litter M., Palmisano L. and Soria J., The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 7 (2006) 127–144.

14. Aungpradit T., Sutthivaiyakit P., Martens D., Sutthivaiyakit S. and Kettrup A. A. F., Photocatalytic degradation of triazophos in aqueous titanium dioxide suspension: Identification of intermediates and degradation pathways, *Journal of Hazardous Materials*, 146 (2007) 204–213.

15. Awasthi M. D. and Prakash N. B., Persistence of chlorpyrifos in soils under different moisture regimes, *Journal of Pestic Science,* 50 (1997) 1-4.

16. Bahnemann D., Photocatalytic water treatment: solar energy applications, *Solar Energy*, 77 (2004) 445–459.

17. Balasubramanian G., Dionysiou D. D. and Makram T., Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water, *Applied Catalysis B: Environmental*, 47 (2004) 73–84.

18. Bandala E.R., Gelover S., Leal T., Arancibia C., Jiménez A. and Estrada C., Solar photocatalytic degradation of Aldrin, *Catalysis Today*, 76 (2002) 189-199.

19. Bandra J., Pulgarin C., Peringer P. and Kiwi J., Chemical (photo-activated) coupled biological homogeneous degradation of p-nitro-o-toluene-sulfonic acid in a flow reactor, *Journal of Photochemistry and Photobiology A: Chemistry*, 111 (1997) 253-263.

20. Bayarri B., Gimenez J., Curco D. and Esplugas S., Photocatalytic degradation of 2,4-dichloophenol by TiO_2/UV: Kinetics, actinometries and models, *Catalysis Today*, 101 (2005) 227-236.

21. Bayer Corp. 1998. Imidacloprid memo to U.S. EPA. June 5, 1998.

22. Blanco J. and Malato S., Compound parabolic concentrator technology development to commercial solar detoxification applications, *Solar Energy*, 67 (1999) 317–330.

23. Bouraie M. M. El., Barbary A. A. El. and Yehia M., Determination of organochlorine pesticide (OCPs) in shallow observation wells from El-Rahawy contaminated area, *Egypt Environmental Research, Engineering and Management*, 3 (2011) 28-38.

24. Carreño J., Rivas, A., Granada A., Jose Lopez-Espinosa M., Mariscal M., Olea N. and Olea-Serrano F., Exposure of young men to organochlorine pesticides in Southern Spain, *Environmental Research*, 103 (2007) 55–61

25. Carey J. H., Lawerence J. and Tosine H. M., Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions, *Bulletin of Environmental Contamination and Toxicology*, 16 (1976) 697-701.

26. Cavalier T. C., Lavy T. L. and Mattice J. D., Persistence of selected pesticides in groundwater samples, *Ground Water*, 29 (1991) 225–231.

27. Center for Science and Environment, Laboratory Results of Bottled Water, www.cseindia.org.hyml/lab/bottled_water_result.htm, New Delhi, 2003.

28. Chan A. H. C., Chan C .K., Barford J. P. and Porter J. F., Solar photocatalytic thin film reactor for the treatment of benzoic acid containing wastewater, *Water Research*, 37 (2003) 1125–1135.

29. Chatzisymeon E., Stypas E., Boosios S., Xekoukoulotakis N. P. and Mantzavinos D., Photocatalytic treatment of black table olive processing wastewater, *Journal of Hazardous Materials*, 154 (2008) 1090-1097.

30. Chatterjee D. and Dasgupta S., Visible light induced photocatalytic degradation of organic pollutants, *Journal of Photochemistry and Photobiology A: Chemistry*, 6 (2005) 186-205.

31. Chatterjee D., Gupta S. D. and Rao N. N., Visible light assisted photodegradation of halocarbons on the dye modified TiO_2 surface using visible light, *Solar Energy Materials and Solar Cells*, 90 (2006) 1013-1020.

32. Chiou C. S., Degradation of di-n-butyl phthalate using photoreactor packed with TiO_2 immobilized on glass beads, *Journal of Hazardous Materials B*, 137 (2006) 1123–1129.

33. Chin M. L., Abdul R. M. and Bhatia S., Performance of photocatalytic reactors using immobilized TiO2 film for the degradation of phenol and methylene blue dye present in water stream, *Chemosphere*, 57 (2004) 547–554.

34. Chiron S., Fernandez A. A., Rodriguez A. and Garcia C. E., Pesticide chemical oxidation: state-of-the-art, *Water Research*, 34 (2000) 366–377.

35. Choi W. and Hoffmann M. R., Novel photocatalytic mechanism for $CHCl_3$, $CHBr_3$ and $CClCO_2$ degradation and the fate of photogenerated trihalomethyl radicals on TiO_2, *Environmental Science and Technology*, 37 (1997) 89-95.

36. Clark G. and Allen C.P., The estimation of atmospheric radiation for clear and cloudy skies, *Proceedings of the Second National Passive Solar Conference*, Philadelphia, Part.2, (1978) 676.

37. Crittenden J. C., Trussell R. R., Hand D. W., Howe K. J. and Tchobanoglous G., *Water Treatment: Principles and Design*, 2nd ed., Wiley, New Jersey, 2005.

38. Daneshvar N., Salari D., Niaei A., Rasoulifard, M. H. and Khataee, A. R., Immobilization of TiO_2 nanopowder on glass beads for the photocatalytic decolorization of an azo dye C.I. Direct Red 23, *Journal of Environmental Science and Health A*, 40 (2005) 1605–1617.

39. Deepu D., George I. A. and Peter J. V., Toxicology of the newer neonicotinoid insecticides: Imidacloprid poisoning in a human, *Clinical Toxicology*, 45 (2007) 485-486.

40. Department of the Environment, *Pesticides in Water Supplies*, London, 1989 (DoE Reference: WS/45/1/1).

41. Dhaliwal G. S. and Singh B., Eds., *Pesticides: Their Ecological Impact in Developing Countries*, Commonwealth Publishers, New Delhi, 1993.

42. Doll T. E. and Frimmel F. H., Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water, *Catalysis Today*, 101 (2005) 195–202.

43. Dubey S. K., Kumar A., Srivastava P. and Anita R., Solar photo-catalytic treatment of textile wastewater for biodegradability enhancement I, *Journal of Environmental Engineering*, 1 (2009) 152-164.

44. Duffie J. A. and Beckman W. A., *Solar Engineering of Thermal Processes*, 3rd ed. John Wiley and Sons Inc, New Jersey, 2006.

45. El-Hajjouji H., Barje F., Pinelli E., Baily J. R., Richard C., Winterton P., Revel J. C. and Hafidi M., Photochemical UV/TiO2 treatment of olive mill wastewater (OMW), *Bioresource Technology*, 99 (2008) 7264-7269.

46. Esplugas S., Gimenez J., Contreras S., Pascual E. and Rodriguez M., Comparison of different AOP for phenol degradation, *Water Research*, 36 (2002) 1034-1042.

47. Evgenidou E., Fytianos K. and Poulios I., Photocatlytic oxidation of dimethoate in aqueous solutions, *Journal of Photochemistry and Photobiology A: Chemistry*, 175 (2005) 29–38.

48. Evgenidou E., Bizani E., Christophoridis C. and Fytianos K., Heterogeneous photocatalytic degradation of prometryn in aqueous solutions under UV-Vis irradiation, *Chemosphere***,** 68 (2007) 1877-1882**.**

49. Fabiyi M. E. and Skelton R .L., Photocatalytic mineralisation of methylene blue using buoyant TiO_2-coated polystyrene beads, *Journal of Photochemistry and Photobiology A: Chemistry*, 132 (2000) 121–128.

50. Farah J., Pesticide Policies in Developing Countries: Do They Encourage Excessive Use? *World Bank Discussion Papers* 238, The World Bank, Washington DC, (1994) 42.

51. Fares A. A., Momani F. A., Shawaqfeh A. T. and Shawaqfeh, M. S., Solar wastewater treatment plant for aqueous solution of pesticide, *Solar Energy*, 81 (2007) 1213-1218.

52. Feitz A. J., Boyden B. H. and Waite T. D., Evaluation of two solar pilot scale fixed-bed photocatalytic reactors, *Water Research*, 34 (2000) 3927–3932.

53. Fenga C. F., Xudong Y. X. and Qiong W. Q., Antifungal capability of TiO_2 coated film on moist wood, *Building and Environment*, 44 (2009) 1088–1093.

54. Fenton, H. J. H., Oxidation of tartaric acid in presence of iron, *Journal of the Chemical Society*, 65 (1894) 899-910.

55. Fossen M., Environmental Fate of Imidiacloprid; Department of Pesticide Regulation, Environmental Monitoring: Sacramento, CA, 2006.

56. Fujishima A., Hashimoto K. and Watanabe T., *TiO_2 Photocatalysis: Fundamentals and Applications*, Tokyo Bkc, 1999.

57. Fujishima A., Rao T. N. and Tryk D. A., Titanium dioxide photocatalysis, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 1 (2000)1–21.

58. Giornelli T., Thesis (PhD), Univ. Tech. Compiègne, in French (2004).

59. Glaze W. H., Kang J. W. and Chapin D. H., Chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, *Ozone Science and Engineering*, 9 (1987) 335-352.

60. Gogate P. R. and Pandit A. B., A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, *Advances in. Environmental Research*, 8 (2004) 501-551

61. Gogate P. R. and Pandit A. B., A review of imperative technologies for wastewater treatment II: Hybrid methods, *Advances in Environmental Research*, 8 (2004) 553-597.

62. Gora A., Toepfer B., Puddu V. and Puma G. L., Photocatalytic oxidation of herbicides in single-component and multicomponent systems: Reaction kinetics analysis, *Applied Catalysis B: Environmental*, 65 (2006) 1–10.

63. Gupta S., Gajbhiye V. T. and Agnihotri N. P., Leaching behavior of imidacloprid formulations in soil, *Bulletin of Environmental Contamination and Toxicology*, 68 (2002) 502-508

64. Guillard C., Disdier J., Monnet C., Dussaud J., Malato S., Blanco J., Maldonado M. I. and Herrmann J. M., Solar efficiency of a new deposited titaniaphotocatalyst: chlorophenol, pesticide and dye removal applications, *Applied Catalysis B: Environmental*, 46 (2003) 319–332.

65. Harp D.L., *Total Organic Carbon* (Direct Method). U.S. Patent 6, 368, 870, April 2009**.**

66. Han S. T., Li J., Xi H., Xu D., Zuo Y. and Zhang J., Photocatalytic decomposition of acephate in irradiated TiO_2 suspensions, *Journal of Hazardous Materials*, 163 (2009) 1165-1172.

67. Haque M. M. and Muneer M., Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspensions of titanium dioxide, *Journal of. Environmental Management*, 69 (2003) 169-176.

68. Hayes W. J. and Laws E. R., *Handbook of Pesticide Toxicology*, Academic Press, New York 1991.

69. Hegazy A. A., Optimizing the thermohydraulic performance of flat-plate solar air heaters operating with fixed/variable pumping power, *Renewable Energy*, 18 (1999) 283-304.

70. Herrmann J. M., Guillard C., Arguello M., Agüera A., Tejedor A., Piedra L. and Fernández A. A., Photocatalytic degradation of pesticide pirimiphos-methyl determination of the reaction pathway and identification of intermediate products by various analytical methods, *Catalysis Today*, 54 (1999) 353–367.

71. Herrmann J. M., Heterogeneous photocatalysis: fundamentals and applications to removal of various types of aqueous pollutants, *Catalysis Today*, 53 (1999) 115-129.

72. Hoffmann M. R., Martin S. T., Choi W. and Bahnemann D. W., Environmental applications of semiconductor photocatalysis, *Chemical Reviews*, 95 (1995) 69-96.

73. Hughes I. and Wood H. F., Risk Assessment of Mixtures of Pesticides and Similar Substances. Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment. Hughes, I. & Wood, H.F. (Ed.), 1-298, Food Standards Agency (2002).

74. Hussain A. and Nick S., Klnetlc studies in heterogeneous photocatalysis, photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TIO, supported on a glass matrix, *The Journal of Physical Chemistry*, 92 (1988) 5726-5731.

75. Inel Y. and Okte A., Photocatalytic degradation of malonic acid in aqueous suspensions of TiO_2: An initial kinetic investigation of CO_2 photogeneration, *Journal of Photochemistry and Photobiology A: Chemistry*, 96 (1996) 175-180.

76. Jannot Y. and Coulibaly Y., Radiative heat transfer in a solar air heater covered with a plastic film, *Solar Energy*, 60 (1997) 35-40.

77. Johnen B. G. and Iwan J., Results and implications from monitoring German raw water forresidues of a wide range of pesticides, *Brighton Crop Protection Conference, Pesticide Discussion*, 1 (1988) 319-328.

78. Kabra S. G., *Independent Study on Pesticide Use and NTDs*, Indian Institute of Health Management and Research, Jaipur, India, 2000.

79. Kamble S. P., Sawant S. B. and Pangarkar V. G., Photocatalytic mineralization of phenoxyacetic acid using concentrated solar radiation and titanium dioxide in slurry photoreactor, *Chemical Engineering Research and Design*, 84 (2006) 355–362.

80. Kannan K., Tanabe S., Ramesh A., Subramanian A. N. and Tatsukawa R., Persistent organochlorine residues in foodstuffs from India and their implications on human dietary exposure, *Journal of Agriculture and Food Chemistry*, 40 (1992) 518–524.

81. Kannan K., Tanabe S,, Giesy J. P. and Tatsukawa R., Organochlorine pesticides and polychlorinated biphenyls in foodstuffs from Asian and Oceanic countries, *Reviews of Environmental Contamination and Toxicology*, 152 (1997) 1–55.

82. Karunakaran C.O., The Kerala food poisoning, *Journal of Indian Medical Association*, 31 (1958) 204.

83. Kawata, K., Behavior of Aerial Applied 4,5,6,7-tetrachlorophthalide in Air, Water and Soil, *Fungicides: Chemistry, Environmental Impact and Health Effects*, De Costa P. and Bezerra P. (Editors), Nova Science Publishers, Hauppauge, NY, USA, (2009) 1-12 .

84. Kitsiou V., Filippidis N., Mantzavinos D. and Poulios I., Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in aqueous solutions, *Applied Catalysis B: Environmental* 86 (2009) 27–35.

85. Konstantinou I. K. and Albanis T. A., Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, *Applied. Catalysis B*, 1310 (2002) 1-17.

86. Kositzi M., Antoniadis A. and Poulios I., Solar photocatalytic treatment of simulated dye stuff effluents, *Solar Energy*, 77 (2004) 591–600.

87. Kuo H. W., Yung H. H., Ming Y. C. and Chen Y. C., Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution, *Applied Catalysis B: Environmental*, 21 (1999) 1-8.

88. Kuburovica N., Todorovicb M., Raicevicb, V., Orlovica A., Jovanovicc L., Nikolica, J., Kuburovicd V., Drmanica S. and Solevice T., Removal of methyl tertiary butyl ether from wastewaters using photolytic, photocatalytic and microbiological degradation processes. *Desalination*, 213 (2007) 123–128.

89. Kulshrestha G. and Muckerjee S. K., The photochemical decomposition of the herbicide isoproturon, *Pesticide Science*, 17 (1986) 489-494.

90. Lapertot M., Ebrahimi S., Dazio S., Rubinelli A. and Pulgarin C., Photo-Fenton and biological integrated process for degradation of a mixture of pesticides, *Journal of Photochemistry and Photobiology A: Chemistry*, 186 (2007) 34–40.

91. Laoufi N. A., Tassalit D. and Bentahar F., The degradation of phenol in water solution by TiO2 photocatalysis in a helical reactor, *Global NEST Journal*, (2008) (in press).

92. Lazar M. A., Varghese S. and Nair S. S., Photocatalytic water treatment by titanium dioxide: Recent updates, *Catalysts*, 2 (2012) 572-601.

93. Leyva E., Moctezuma E., Ruiz M. G. and Torres L. M., Photo-degradation of phenol and 4-chlorophenol by $BaO\text{-}Li_2O\text{-}TiO_2$ catalysis, *Catalysis Today*, 40 (1998) 367-376.

94. Liu W. P., Gan J., Schlenk D. and Jury W. A.., Enantioselectivity in environmental safety of current chiral insecticides, *PNAS (USA)* 103 (2005) 701-706.

95. Luna D., Jannot Y. and Nadeau J. P., An oriented-design simplified model for the efficiency of a flat plate solar air collector, *Applied Thermal Engineering*, 30 (2010) 2808-2814.

96. Macounová K., Urban J., Krýsová H., Krýsa J., Jirkovský J. and Ludvık J., Photodegradation of metamitron (4-amino-6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one) on TiO2, *Journal of Photochemistry and Photobiology A: Chemistry*, 140 (2001) 93–98.

97. Madani M. E., Guillard C., Pe´rol N., Chovelon J. M., Azzouzi M. E., Zrineh A. and Herrmann J .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, *Applid Catalysis B: Environmental*, 65 (2006) 70–76.

98. Mahmoodi N. M., Arami M. and Limaeei N. Y., Photocatalytic degradation of triazinic ring- containing azo dye (reactive red 198) by using immobilized TiO_2 photoreactor: Bench scale study, *Journal of Hazardous Materials*, 133 (2006) 113–118.

99. Mahmoodi N. M., Arami M., Limaee N. Y. and Gharanjig K., Photocatalytic degradation of agricultural *N*-heterocyclic organic pollutants using immobilized nanoparticles of titania., *Journal of Hazardous Materials*, 145 (2007) 65–71.

100. Malato S., Blanco J., Vidal A., Richter C., Photocatalysis with solar energy at a pilot-plant scale: An overview, *Applied Catalysis*, 37 (2002) 1–15.

101. Malato S., Blanco J., Estrada C., Bandala E .R. and Peñuela G., Pesticide degradation. In: Contaminants removal by heterogeneous photocatalysis. Blesa, M.A.; Sánchez B. (Ed) Editorial CIEMAT, Madrid, Spain. (In Spanish) (2004).

102. Malato S., Fern_andez-Ib_a~ne, P., Maldonado M. I., Blanco J. and Gernjak W., Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, *Catalysis Today*, 147 (2009) 1–59.

103. Maldonado M. I., Passarinho P. C., Oller I., Gernjak F. P., Blanco J. and Malato S., Photocatalytic degradation of EU priority substances: A comparison between TiO_2 and Fenton plus photo-Fenton in a solar pilot plant. *Journal of Photochemistry and Photobiology A: Chemistry*, 185 (2007) 354–363.

104. Mathur S. C., Future of Indian pesticides industry in next millennium, *Pesticide Information*, 24 (1999) 9–23.

105. Matthews R. W., Photooxidation of organic material in aqueous suspensions of titanium dioxide, *Water Research*, 20 (1986) 569–578.

106. Matthews R. W., Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide, *Journal of Catalysis*, 111 (1988) 264-272.

107. Marco A., Esplugas S. and Saum G., How and why to combine chemical and biological processes for wastewater treatment, *Water Science and Technology*, 35 (1997) 321–327.

108. Marer P. F., *The Safe and Effective Use of Pesticides. Pesticide Application Compendium 1*, University of California, Statewide Integrated Pest Management Project, Division of Agriculture and Natural Resources, Publications 3324 (1988).

109. Marugan J., Van Grieken R., Cassano A. E. and Alfano O. M., Intrinsic kinetic modeling with explicit radiation absorption effects of the photocatalytic oxidation of cyanide with TiO_2 and silica-supported TiO_2 suspensions, *Applied Catalysis B: Environmental*, 85 (2008) 48−60.

110. Marugan J., Van G. R., Cassano A. E. and Alfano O. M., Scaling-up of slurry reactors for the photocatalytic oxidation of cyanide with TiO_2 and silica-supported TiO_2 suspensions, *Catalysis Today*, 144 (2009) 87−93.

111. McLoughlin O. A., Iba´n˜ezb P. F., Gernjak W., Malato S. and Gill L. W., Photocatalytic disinfection of water using low cost compound parabolic collectors, *Solar Energy*, 77 (2004) 625–633.

112. Mehrotra K., Yablonsky G. S. and Ray A. K., Macro kinetic studies for photocatalytic degradation of benzoic acid in immobilized systems, *Chemosphere*, 60 (2005) 1427-1436.

113. Meijers R. T., Oderwald M. E. J., Nuhn P. A. N. M. and Kruithof J. C., Degradation of pesticides by ozonation and advanced oxidation, *Ozone Science and Engineering*, 17 (1995) 673–686.

114. Mencher J. P., Agricultural labor and pesticides in rice growing regions of India: Some health considerations, *Economic and Political Weekly*, XXVI (39) (1991) 2263-68.

115. Minton N. A. and Murray V. S. G., A review of organophosphate poisoning, *Medical Toxicology*, 3 (1988) 350-375.

116. Miranda N. S., Photocatalytic degradation of emerging contaminants in municipal wastewater, *Applied Catalysis B: Environmental*, 103 (2011) 294–301.

117. Momani Al. F. A., Impact of photo-oxidation technology on the aqueous solutions of nitrobenzene: degradation efficiency and biodegradability enhancement, *Journal of Photochemistry and Photobiology. A: Chemistry*, 179 (2006) 184–192.

118. Momani F. A. A., Shawaqfeh A. T. and Shawaqfeh M. S., Solar wastewater treatment plant for aqueous solution of pesticide, *Solar Energy*, 81 (2007) 1213-1218.

119. Motegh M., Ommen J. R., Appel P. W. and Kreutzer M. T., Scale-Up study of a multiphase photocatalytic reactor-degradation of cyanide in water over TiO_2, *Environmental Science and Technology*, 48 (2014) 1574−158.

120. Mozia S., Tomaszewska M. and Antoni, M. W., Photodegradation of azo dye Acid Red 18 in a quartz labyrinth flow reactor with immobilized TiO_2 bed, *Dyes and Pigments*, 75 (2007) 60-66.

121. Mukherjee P. S. and Ray A. K., Major challenges in the design of a large-scale photocatalytic reactor for water treatment, *Chemical Engineering and Technology*, 22 (1999) 253-260.

122. Munoz I., Peral J., Ayllon J. A., Malato S., Passarinho P. and Domenech X., Life cycle assessment of a coupled solar photocatalytic-biological process for wastewater treatment, *Water Research,* 40 (2006) 3533-3540.

123. Muneer M. and Bahnemann D., Semiconductor-mediated photocatalysed degradation of two selected pesticide derivatives, terbacil and 2,4,5-tribromoimidazole, in aqueous suspensions, *Applied Catalysis B: Environmental*, 36 (2002) 95-111.

124. Muruganandham M. and Swaminathan M., Solar photocatalytic degradation of a reactive azo dye in TiO2 suspension, *Solar Energy Material and Solar Cells*, 81 (2004) 439-457.

125. Nogueira R. F. P. and Jardim W. F., TiO_2-fixed-bed reactor for water decontamination using solar light, *Solar Energy*, 56 (1996) 471–477.

126. Noorjahan M., Reddy M. P, Kumari V. D, Lavédrine B., Boule P. and Subrahmanyam M., Photocatalytic degradation of H-acid over a novel TiO2 thin film fixed bed reactor and in aqueous suspensions, *Journal of Photochemistry and Photobiology A: Chemistry*, 156 (2003) 179–187.

127. Oller I., Gernjak W., Maldonado M. I., Pérez-E. L. A., Sánchez-P. J. A. and Malato S., Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale, *Journal of Hazardous Materials*, 138 (2006) 507-17.

128. Oller I., Malato S., Sanchez P. J. A., Gernjak W., Maldonado M. I., Estrada P. L. A. and Pulgarin C., A combined solar photocatalytic-biological system for the mineralization of an industrial pollutant at pilot scale, *Catalysis Today*, 122 **(**2007) 150-159.

129. Parra S., Sarria V., Malato S., Péringer P. and Pulgarin C., Photochemical versus coupled photochemical–biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon, *Applied Catalysis B: Environ*mental, 27 (2000) 153–168.

130. Parra S., Malato S., Blanco J., Péringer P. and Pulgarin C., Concentrating versus non-concentrating reactors for solar photocatalytic degradation of p-nitrotoluene-o-sulfonic acid, *Water Science and Technology*, 44 (2001) 219–227.

131. Parra S., Malato S. and Pulgarin C., New integrated photocatalytic-biological flow system using supported TiO_2 and fixed bacteria for the mineralization of isoproturon, *Applied Catalysis B: Environmental*, 36 (2002) 131–144.

132. 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.

133. Paunero I. E., Mitidieri M., Ferratto J., Giuliani S., Bulacio L., Panelo M., Amoia P., Strassera M. E., Granitto G., del Pino M., Martínez S., Fortunato N., Tangorra M., Andreau R., Garbi M. and Martínez-Quintana O., Identifying the primary types of accidents that occur to horticultural workers in Argentina, *Agricultura, Sociedad y Desarrollo*, 6 (2009) 177-182.

134. Percherancier J. P., Chapelon R. and Pouyet B., Semiconductor sensitized photodegradation of pesticides in water: the case of carbetamide, *Journal of Photochemistry and Photobiology A: Chemistry*, 87 (1995) 261-266.

135. Pozzo R. L., Baltanas M. A. and Cassano A. E., Supported titanium oxide as photocatalyst in water decontamination: State of the art, *Catalysis Today*, 39 (1997) 219-231.

136. Puma G. L. and Yue P. L., A novel fountain photocatalytic reactor for water treatment and purification: Modeling & design, *Industrial and Engineering Chemistry Research*, 40 (2001) 5162–5169.

137. Puma G. L., Toepfer B. and Gora A., Photocatalytic oxidation of multicomponent systems of herbicides: Scale-up of laboratory kinetics rate data to plant scale, *Catalysis Today*, 124 (2007) 124–132.

138. Radjenovic J. S., Solar photocatalytic degradation of persistent pharmaceuticals at pilot-scale: kinetics and characterization of major intermediate products, *Applied Catalysis B: Environmental*, 89 (2009) 255-264.

139. Raipulis J., Maija M. and Balode M., Toxicity and genotoxicity testing of roundup, *Proceedings of the Latvian Academy of Sciences Section B*, 63 (2009) 29–32.

140. Rajendran S., Environment and Health Aspects of Pesticides Use in Indian Agriculture in Martin J. B., Suresh V. M. and Kumaran T. V., eds., Proceedings of the 3rd International Conference on Environment and Health, Chennai, India, 15-17 December, 2003.

141. Rao Rama C. A., Srinivasa R. M., Alaiah P., Malathi B. and Reddy Y. V. R., An economic analysis of adoption of integrated pest management in groundnut, *Indian Journal of Agricultural Economics*, 63 (1) (2008) 97-107.

142. Rao K., Venkata S., Rachel A., Subrahmanyam M. and Boule P., Immobilization of TiO2 on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants, *Applied Catalysis B: Environmental*, 46 (2003) 77–85.

143. Rao N. N. and Chaturvedi C. K., Novel pebble bed photocatalytic reactor for solar treatment of textile wastewater, *Chemical Engineering Journal*, 184 (2012) 90– 97.

144. Raquel F. P., Nogueira and Wilson F. J., TiO_2- fixed bed reactor for water decontamination using solar light, *Solar Energy*, 56 (1996) 471-477.

145. Ray A. K. and Beenackers A. C. M., Novel photocatalytic reactors for water treatment, *AIChE Journal*, 44 (1998) 477–483.

146. Ray A. K., Design, modeling and experimentation of a new large-scale photocatalytic reactor for water treatment, *Chemical Engineering Science*, 54 (1999) 3113-3125.

147. Reddy K. S. and Ravikumar K., Solar collector field design and viability analysis of stand-alone parabolic trough power plants for Indian conditions, *Energy for Sustainable Development*, 16 (2012) 456–470.

148. Reigart J. R. and Roberts J. R., Recognition and Management of Pesticide Poisonings (6^{th} ed.), *United States Environmental Protection Agency Publication*, (2013) EPA-735K-13001.

149. Reupert R. and Ploeger E., Determination of N-herbicides in groundwater, drinking-water and surface water: analytical method and results, *Vom Wasser*, 72 (1989) 211-233.

150. Roche P. and Prados M., Removal of Pesticides by use of ozone or hydrogen Peroxide/ozone, *Ozone Science and Engineering*, 17 (1995) 657-672

151. Sandermann H., Heller W., Hertkorn N., Hoque E., Pieper D. and Winkler R., A new intermediate in the mineralization of 3,4-dichloroaniline by the white rot fungus phanerochaete chrysosporium, *Applied and Environmental Microbiology*, 64 (1998) 3305–3312.

152. Stapleton D. R., Mantzavinos D. and Papadaki M., Photolytic (UVC) and photocatalyic (UVC/TiO_2) decomposition of pyridines, *Journal of Hazardous Materials*, 146 (2007) 640–645.

153. Sarria V., Parra S., Adler N., Peringer P., Benitez N. and Pulgarin, C., Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds, *Catalysis Today*, 76 (2002) 301-315.

154. Sarria V., Kenfack S., Guillod O. and Pulgarin C., An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants, *Journal of Photochemistry and Photobiology A: Chemistry*, 159 (2003) 89–99.

155. Schroeder M. E. and Flattum R. F., The mode of action and neurotoxic properties of the nitroethylene heterocycle insecticides, *Pesticide Biochemistry and Physiology*, 22 (1984) 148-160.

156. Schuelein J., Glaessgen W. E., Hertkorn N., Schroeder P., Sandermann H. and Kettrup A., Detection and identification of the herbicide isoproturon and its metabolites in field samples after a heavy rainfall event, *International Journal of Environmental Analytical Chemistry*, 65 (1996) 93–202.

157. Senthil K. K, Kannan K., Subramanian A and Tanabe S., Accumulation of organochlorine pesticides and polychlorinated biphenylsin sediments, aquatic organisms, birds, bird eggs and bat collected from south India, *Environmental Science and Pollution Research*, 7 (2000) 1–13.

158. Serpon N. and E. Pelizzetti, Eds, *Photocatalysis. Fundamentals and Applications*, Wiley, New York, 1989.

159. Sharma, M. V. P., Kumari V. D. and Subrahmanyam M., Photocatalytic degradation of isoproturon herbicide over TiO_2/Al-MCM-41 composite systems using solar light, *Chemosphere*, 72 (2008a) 644–65.

160. Sharma M. V. P., Kumari V. D. and Subrahmanyam M., TiO_2 supported over SBA-15: An efficient photocatalyst for the pesticide degradation using solar light. *Chemosphere*, 73 (2008b) 1562-1569.

161. Sharma S. K., Bhunia H. and Bajpai P. K., Photocatalytic decolorization kinetics and mineralization of reactive black 5 aqueous solution by UV/TiO2 nanoparticles, *Clean-Soil, Air, Wate*r, 40 (2012) 1290–1296.

162. Shifu C. and Gengyu C., Photocatalytic degradation of organophosphorus pesticides using floating photocatalyst TiO_2.SiO_2/beads by sunlight, *Solar Energy*, 79 (2005) 1-9.

163. Sraw A., Wanchoo R. K. and Toor A. P., Optimization and kinetic studies for degradation of insecticide monocrotophos using LR grade and P25 TiO_2 under UV/Sunlight conditionsm, *Environmental Progress and Sustainable Energy*, DOI 10.1002/ep.

164. Srinivasan G., Panel for reduced use of chemical pesticides. *Hindu Business Line,* November 5, 1997.

165. Stackelberg P. E., Furlong E. T., Meyer M. T., Zaugg S. D., Henderson A. K. and Reissman D. B., Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water treatment plant, *Science of Total Environ*mental, 329 (2004) 99-113.

166. Starner K. and Goh K. S., Detection of the neonicotinoid insecticide imidacloprid in surface waters of three agricultural regions of California, USA, 2010–2011, *Bulletin of Environmental Contamination and Toxicology*, 88 (2012) 316–321.

167. Stasinakis A. S., Use of selected advanced oxidation processes (AOPs) for wastewater treatment – A mini review , *Global NEST Journal*, 10 (2008) 376-385.

168. Subrahmanyam M., SubbaRao K. V., Rachel A., Boule P., Immobilization of TiO_2 on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants, *Applied Catalysis B: Environmental*, 46 (2003) 77–85.

169. Tennakone K., Tilakaratne C. T. K. and Kottegoda I. R .M., Photocatalytic degradation of organic contaminants in water with TiO_2 supported on polythene films, *Journal of Photochemistry and Photobiology A: Chemistry*, 87 (1995) 177-179.

170. Toor A. P., Verma A.; Singh, V., Jotshi C. K. and Bajpai P. K., Photocatalytic degradation of 3,4 dichlorophenol using TiO_2 in a shallow pond slurry reactor, *Indian Journal of Chemical Technology*, 12 (2005) 75-81**.**

171. Toor A. P., Verma A., Singh V., Jotshi C. K. and Bajpai P. K., Treatment of bleaching effluents from the pulp and paper industry by photocatalytic oxidation, *Tappi Journal* 6 (2007) 9-13**.**

172. Toor A. P., Verma A., Singh V., Jotshi C. K. and Bajpai P. K., Photocatalytic degradation of direct yellow 12 dye using UV/TiO_2 in a shallow pond slurry reactor, *Dyes and Pigments*, 68 (2006) 53-60.

173. U.S. Environmental Protection Agency, 1993. Office of Pesticide Programs, Washington, DC. Biopesticide-Natural Insect Growth Regulators, (accessed Feb 2001). http://www.epa.gov/pesticides/biopesticides/ai/natinsectgrowreg.htm

174. Van Dyck H., Van Strien A. J., Maes D. and Van Swaay C. A. M., Declines in common, widespread butterflies in a landscape under intense human use, *Conservation Biology*, 23 (2009) 957–965.

175. Verma A., Divya D., Toor A. and Srivastava J., Heterogeneous photocatalytic degradation of 2-chloro-4-nitrophenol using slurry and fixed bed reactor, *Environmental Progress and Sustainable Energy*, 2014 (DOI 10.1002/ep.11997)

176. Verma A., Sheorn M. and Toor A. P., Titanium dioxide mediated photocatalytic degradation of malathion in aqueous phase, *Indian Journal of Chemical Technology*, 20 (2013) 46-51.

177. Vigo F. and Cagliari M., Photocatalytic oxidation applied to olive mill wastewaters treatment, *Rivista Italiana Delle Sostanze Grasse*, 76 (1999) 345-353.

178. Wang K. H., Hsiehb Y. H., Choub M. Y., and Changb C. Y. Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution. *Applied Catalysis B: Environmental* 21 (1999) 1-8.

179. Wang H. S., Chen Z. J., Wei W., Man Y. B., Giesy J. P., Du J., Zhang G., Wong C. K. and Wong M. H., Concentrations of organochlorine pesticides (OCPs) in human blood plasma from Hong Kong: markers of exposure and sources from fish, *Environment International*, 54 (2013) 18-25.

180. Wold A., Photocatalytic properties of TiO_2, *Chemistry of Materials*, 5 (1993) 280-283.

181. World Health Organisation, *Health Implications from Monocrotophos Use: A Review of the Evidence in India*. Regional Office for South-East Asia.

182. Worthing C. R., *The Pesticide Manual: A World Compendium*, eighth ed., Published by the British Crop Protection Council Worthing CR, ed. *The Pesticide Manual*, 9th ed. Farnham, British Crop Protection Council, 1991

183. Wyness P., Klausner J. F., Goswami D. Y. and Schanze K. S., Performance of non-concentrating solar photocatalytic oxidation reactors. Part II. Shallow pond configuration, *Journal of Solar Energy Engineering*, 116 (1994) 8–13.

184. Xi W., Geissen S. U. and Vogelpohl A., Solar detoxification of wastewater in a novel aerated cascade photoreactor (ACP), *Water Science and Technology*, 44 (2001) 237–244.

185. Youbin S., Midao W., Chao T., Jing Z. and Dongmei Z, Effect of charcoal amendment on adsorption, leaching and degradation of isoproturon in soils, *Journal of Contaminant Hydrology*, 123 (2010) 75-81.

186. Younes M. and Galal G. H., Pesticides in drinking water - A case study, *Food and Chemical Toxicology*, 38 (2000) S87–S90.

187. Zapata A., Malato S., Sa´nchez P. J. A., Oller I. and Maldonado M. I., Scale-up strategy for a combined solar photo-Fenton/biological system for remediation of pesticide-contaminated water, *Catalysis Today*, 151 (2010) 100–106.

188. 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.

189. Zhu X., Yuan C. and Chen H., Photocatalytic degradation of pesticide pyridaben. 3. In surfactant/TiO_2 aqueous dispersions, *Environmental Science and Technology*, 41 (2007) 263-269.

References cited from weblinks:

- Report of CSE-India (www.cseindia.org.hyml/lab/bottled_water_result.htm)
- Report of NYTimes-Asia (www.nytimes.com/2007/12/04/world/asia/04water.html)
- Report of Tribune-India (www.tribuneindia.com/2008/20080407/jal.html)
- Report of Tribune-India (www.tribuneindia.com/2010/20100729/biz.html)
- Report of Madhya Pradesh Pollution Control Board (http://mpcb.gov.in/healthenvt/punjabhealth.php) .

APPENDIX

Qualitative Analysis Report

Data Filename	SC_1205006-1.d	**Sample Name**	SC_1205006
Sample Type	Sample	**Position**	Vial 82
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 10:50:05 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205007-1.d	**Sample Name**	SC_1205007
Sample Type	Sample	**Position**	Vial 83
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:21:15 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205008-1.d	**Sample Name**	SC_1205008
Sample Type	Sample	**Position**	Vial 84
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:52:25 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

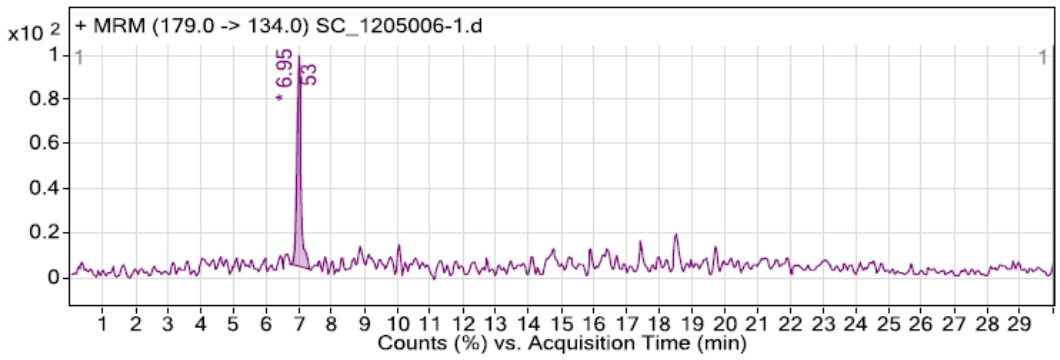
Sample Group **Info.**

Data Filename	Std_1-2.d	**Sample Name**	Std_1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 12:23:36 PM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

User Chromatograms

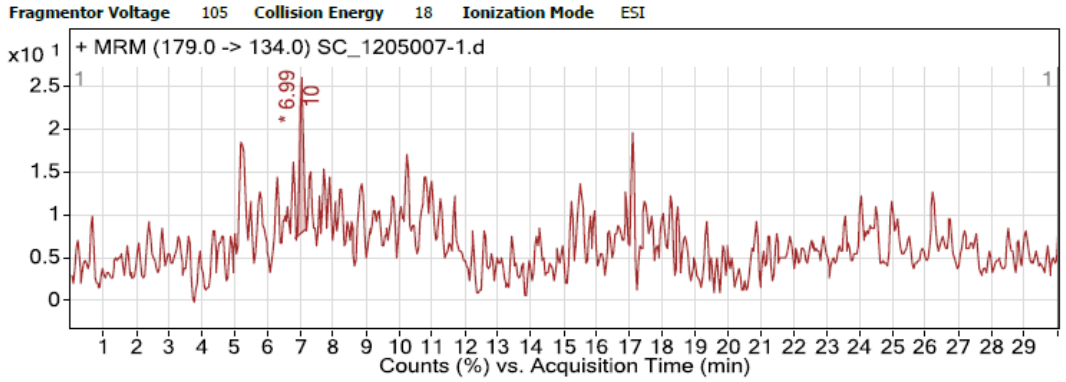
Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



Integration Peak List

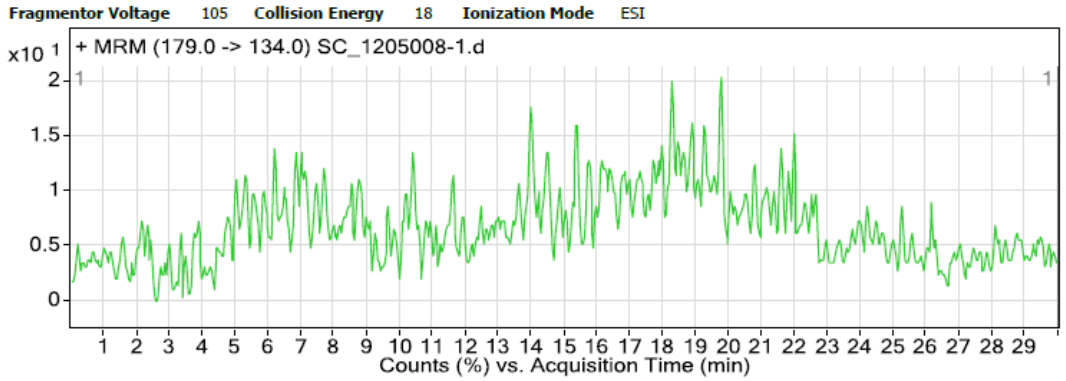
Start	RT	End	Height	Area
6.71	6.95	7.32	5	53

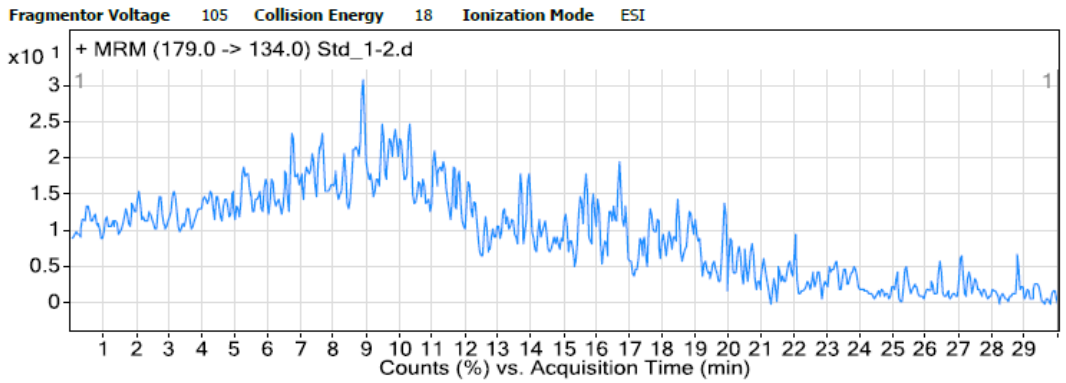
Qualitative Analysis Report



Integration Peak List

Start	RT	End	Height	Area
6.83	6.99	7.15	1	10





Qualitative Analysis Report

Data Filename	SC_1205006-1.d	**Sample Name**	SC_1205006
Sample Type	Sample	**Position**	Vial 82
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 10:50:05 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205007-1.d	**Sample Name**	SC_1205007
Sample Type	Sample	**Position**	Vial 83
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:21:15 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205008-1.d	**Sample Name**	SC_1205008
Sample Type	Sample	**Position**	Vial 84
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:52:25 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

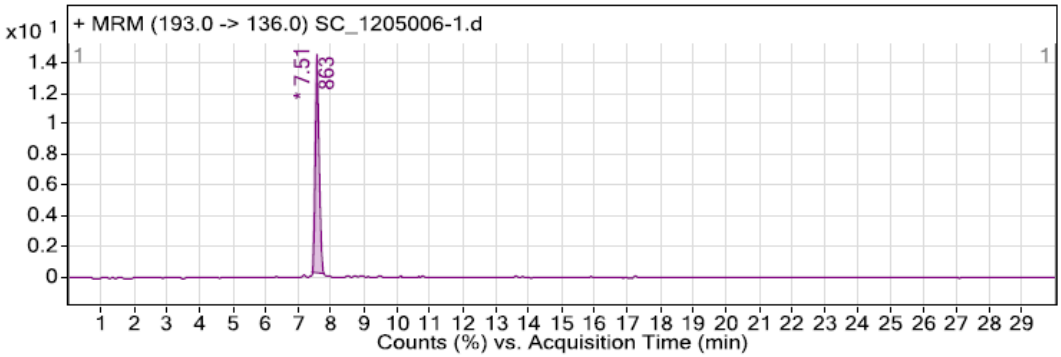
Sample Group **Info.**

Data Filename	Std_1-2.d	**Sample Name**	Std_1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 12:23:36 PM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

User Chromatograms

Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI

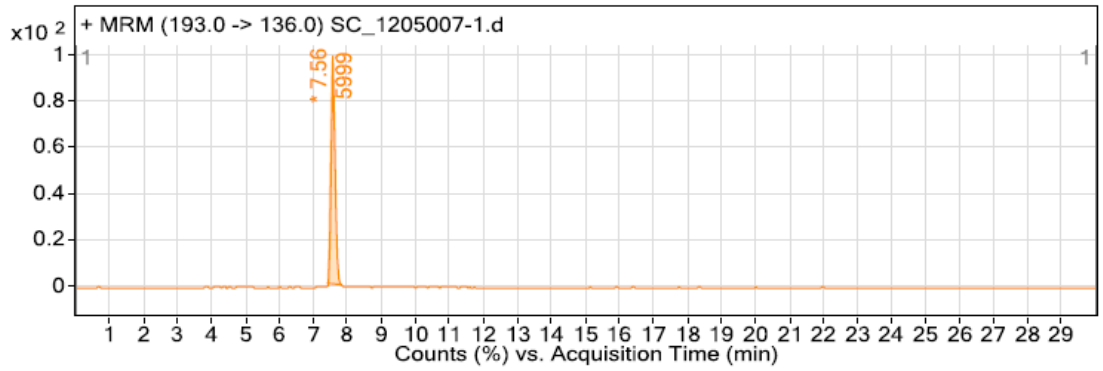


Integration Peak List

Start	RT	End	Height	Area
7.39	7.51	7.76	90	863

Qualitative Analysis Report

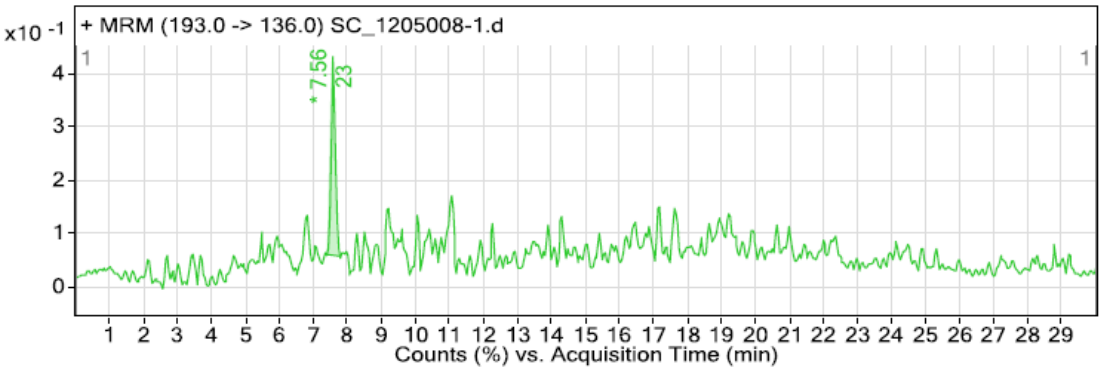
Fragmentor Voltage 105 Collision Energy 18 Ionization Mode ESI



Integration Peak List

Start	RT	End	Height	Area
7.39	7.56	7.84	620	5999

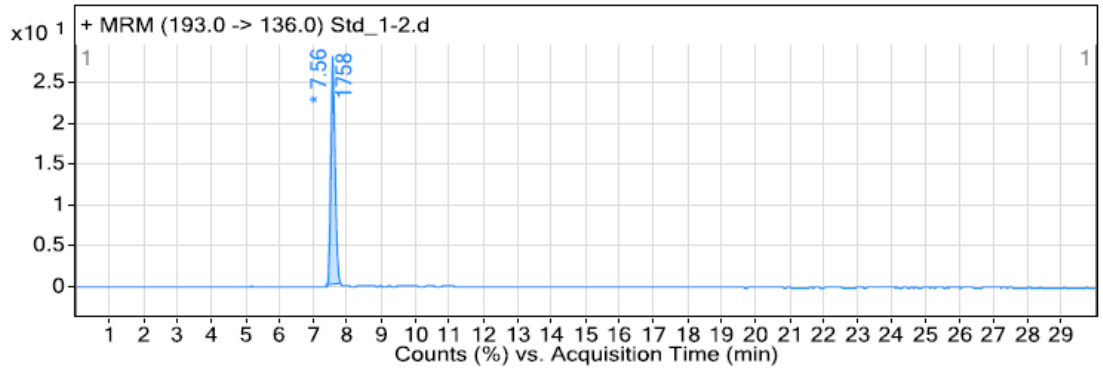
Fragmentor Voltage 105 Collision Energy 18 Ionization Mode ESI



Integration Peak List

Start	RT	End	Height	Area
7.35	7.56	7.76	2	23

Fragmentor Voltage 105 Collision Energy 18 Ionization Mode ESI



Integration Peak List

Start	RT	End	Height	Area
7.35	7.56	7.8	175	1758

Qualitative Analysis Report

Data Filename	SC_1205006-1.d	**Sample Name**	SC_1205006
Sample Type	Sample	**Position**	Vial 82
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 10:50:05 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205007-1.d	**Sample Name**	SC_1205007
Sample Type	Sample	**Position**	Vial 83
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:21:15 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205008-1.d	**Sample Name**	SC_1205008
Sample Type	Sample	**Position**	Vial 84
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:52:25 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

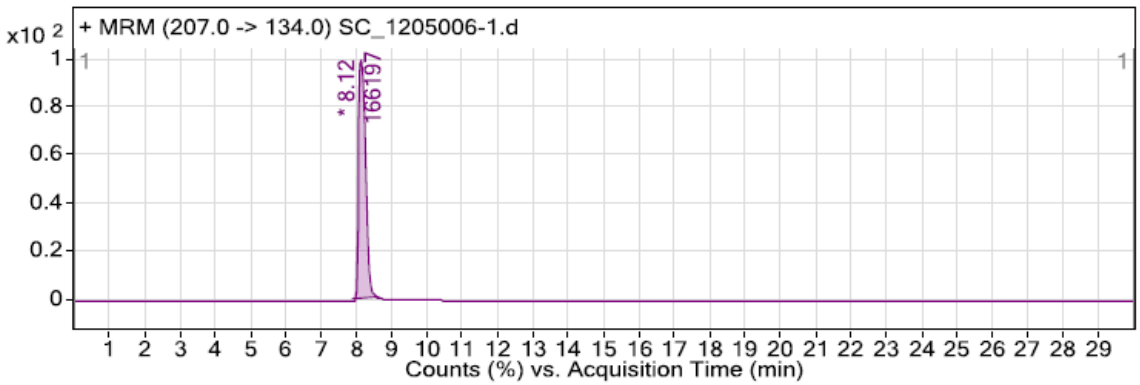
Sample Group **Info.**

Data Filename	Std_1-2.d	**Sample Name**	Std_1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 12:23:36 PM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

User Chromatograms

Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI

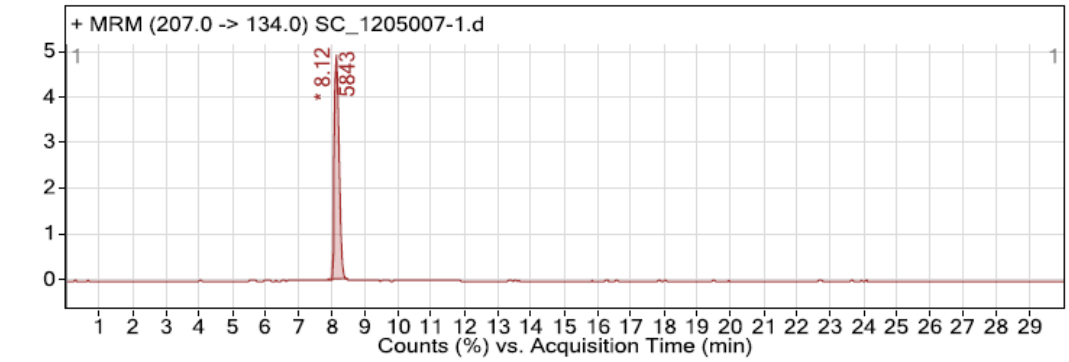


Integration Peak List

Start	RT	End	Height	Area
7.87	8.12	8.65	11795	166197

Qualitative Analysis Report

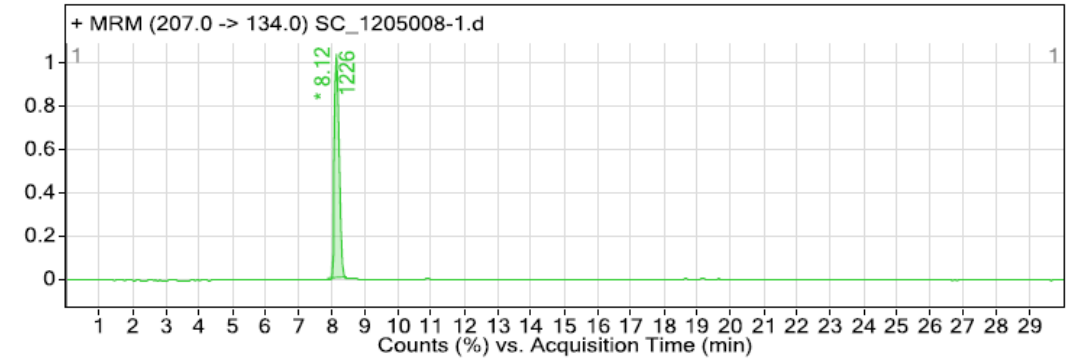
Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
7.87	8.12	8.49	584	5843

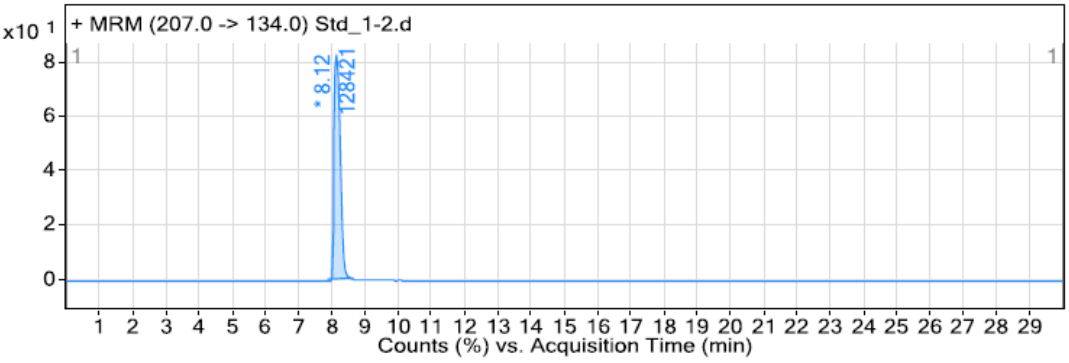
Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
7.87	8.12	8.44	123	1226

Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
7.87	8.12	8.65	9817	128421

Qualitative Analysis Report

Data Filename	SC_1205006-1.d	**Sample Name**	SC_1205006
Sample Type	Sample	**Position**	Vial 82
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 10:50:05 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205007-1.d	**Sample Name**	SC_1205007
Sample Type	Sample	**Position**	Vial 83
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:21:15 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205008-1.d	**Sample Name**	SC_1205008
Sample Type	Sample	**Position**	Vial 84
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:52:25 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

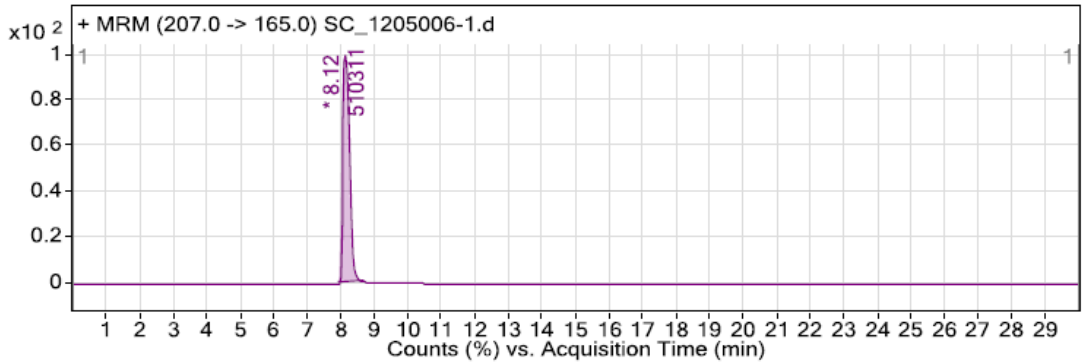
Sample Group **Info.**

Data Filename	Std_1-2.d	**Sample Name**	Std_1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 12:23:36 PM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

User Chromatograms

Fragmentor Voltage 105 **Collision Energy** 8 **Ionization Mode** ESI

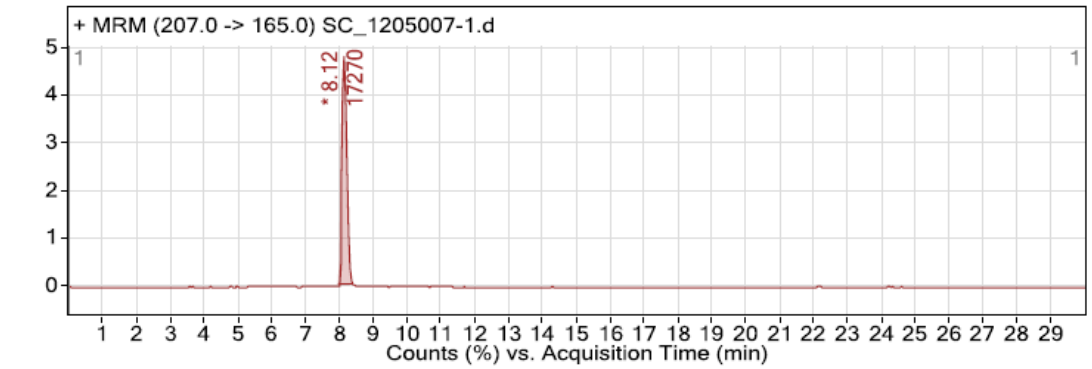


Integration Peak List

Start	RT	End	Height	Area
7.92	8.12	8.69	36256	510311

Qualitative Analysis Report

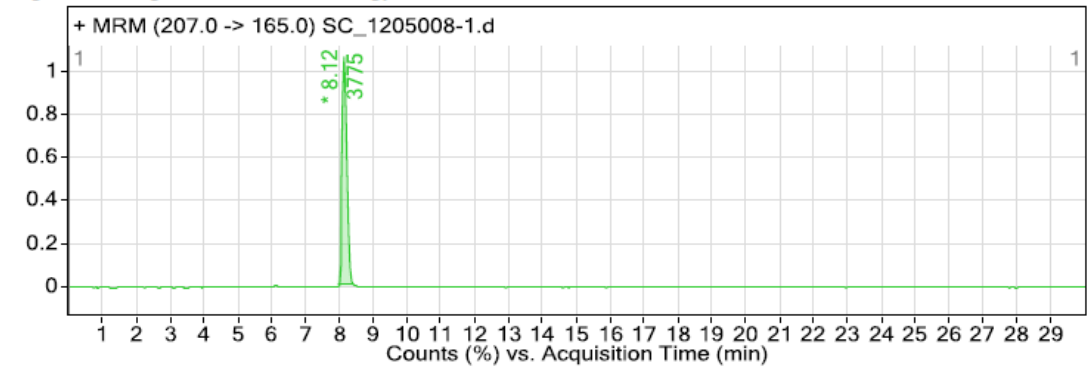
Fragmentor Voltage 105 **Collision Energy** 8 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
7.96	8.12	8.4	1744	17270

Fragmentor Voltage 105 **Collision Energy** 8 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
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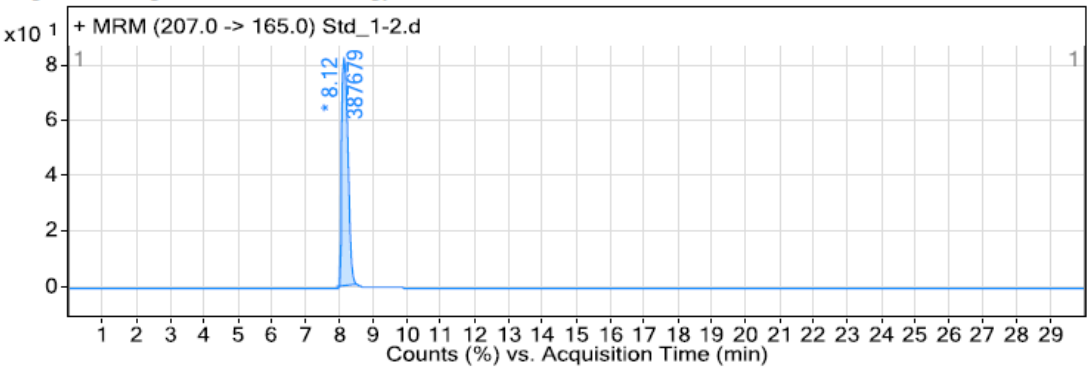
Fragmentor Voltage 105 **Collision Energy** 8 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
7.92	8.12	8.53	30037	387679

Qualitative Analysis Report

Data Filename	SC_1205006-1.d	**Sample Name**	SC_1205006
Sample Type	Sample	**Position**	Vial 82
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 10:50:05 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

Data Filename	SC_1205007-1.d	**Sample Name**	SC_1205007
Sample Type	Sample	**Position**	Vial 83
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:21:15 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

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Sample Type	Sample	**Position**	Vial 84
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 11:52:25 AM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

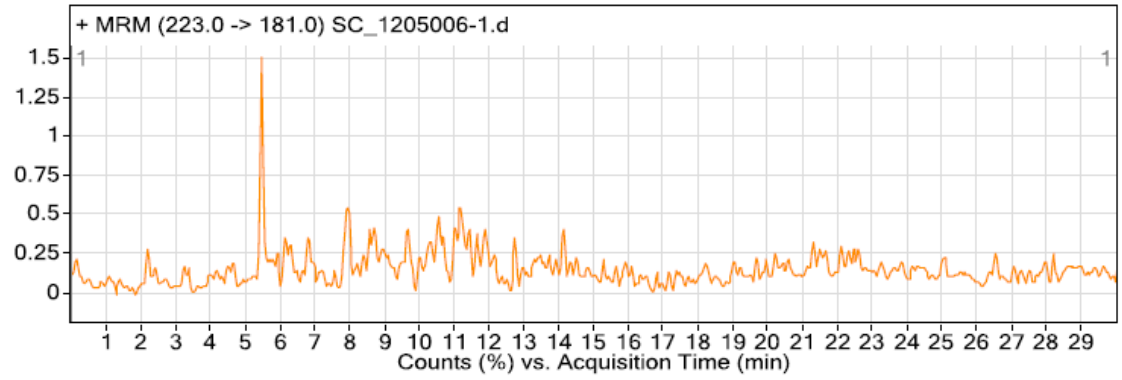
Sample Group **Info.**

Data Filename	Std_1-2.d	**Sample Name**	Std_1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
Acq Method	Isoproturon_Metabolites.m	**Acquired Time**	5/16/2012 12:23:36 PM
IRM Calibration Status	Not Applicable	**DA Method**	Sudan_MRM_F.m
Comment			

Sample Group **Info.**

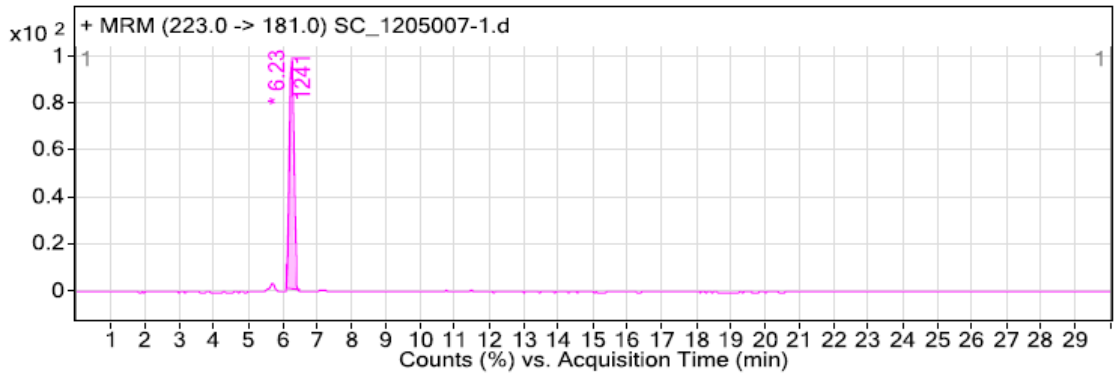
User Chromatograms

Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI

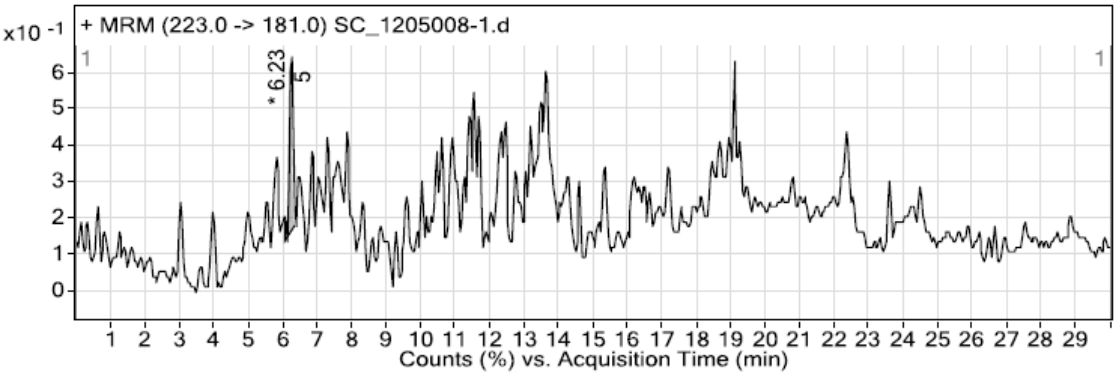
Qualitative Analysis Report



Integration Peak List

Start	RT	End	Height	Area
6.11	6.23	6.52	144	1241

Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



Integration Peak List

Start	RT	End	Height	Area
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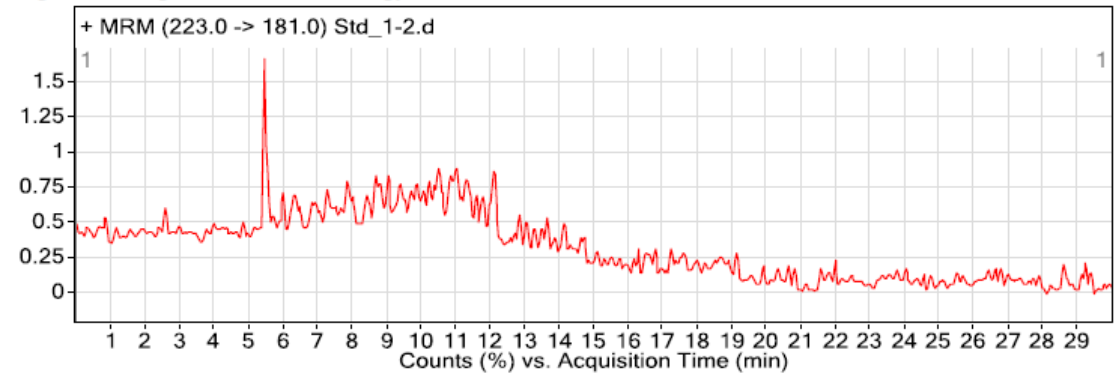
Fragmentor Voltage 105 **Collision Energy** 18 **Ionization Mode** ESI



LIST OF PUBLICATIONS

➢ Published Articles

- Verma, A., Tejo, N. T. P. and Toor, A. P., 2014. An efficient TiO_2 coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies. **Chemosphere**, 109, 7-13.

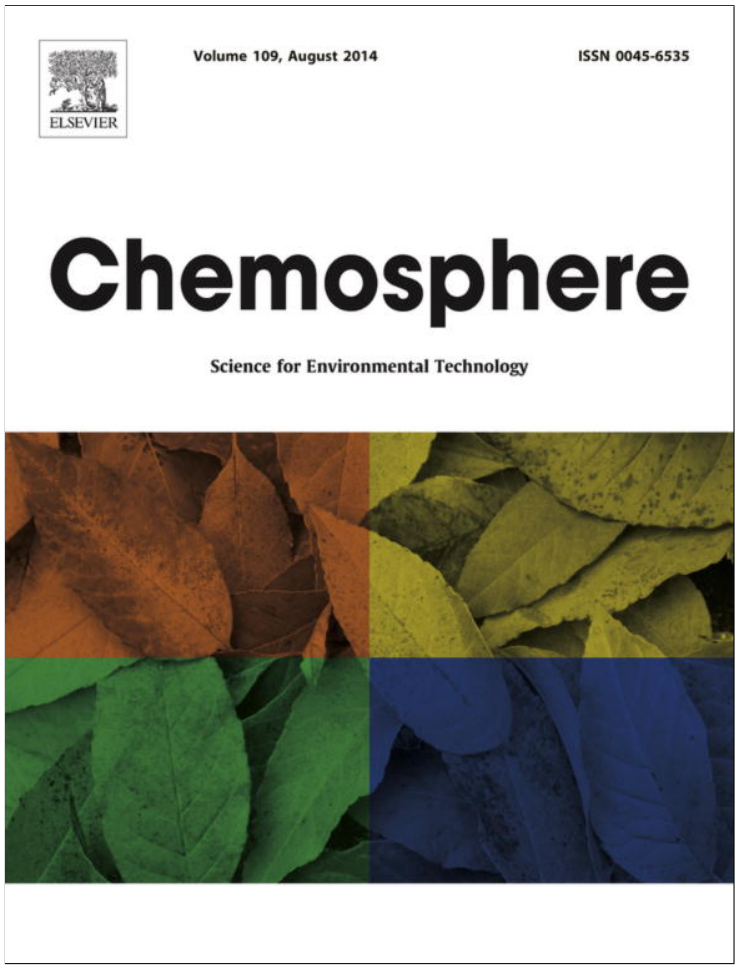
- Verma, A., Tejo, N. T. P. and Toor, A. P., 2014. Photocatalytic degradation of herbicide Isoproturon in TiO_2 aqueous suspensions: Study of reaction intermediates and degradation pathways. **Environ. Prog. Sustain. Energy.** 33 (2), 402-409.

➢ Communicated Articles

- Verma, A., Tejo, N. T. P. and Toor, A. P., Slurry and fixed-bed photocatalytic degradation studies of insecticide Imidacloprid: Lab to pilot-scale (Communicated to Water Research).

➢ Conference Presentations

- Verma, A., Tejo, N. T. P. and Toor, A. P., 2012. Titanium dioxide mediated Photocatalytic Degradation of Isoproturon in Aqueous Suspensions, in Advanced Oxidation Processes (AOP 2012), held at Kottayam, Kerala, October 5-8, 2012.
- Verma, A., Tejo, N. T. P. and Toor, A. P., 2014. Fixed- bed Solar-photocatalytic Reactor for the Degradation of Isoproturon: Lab to pilot scale, in Advanced Oxidation Processes (AOP 2014), held at Munnar, Kerala, September 25-28, 2014.



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journal homepage: www.elsevier.com/locate/chemosphere

An efficient TiO_2 coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies

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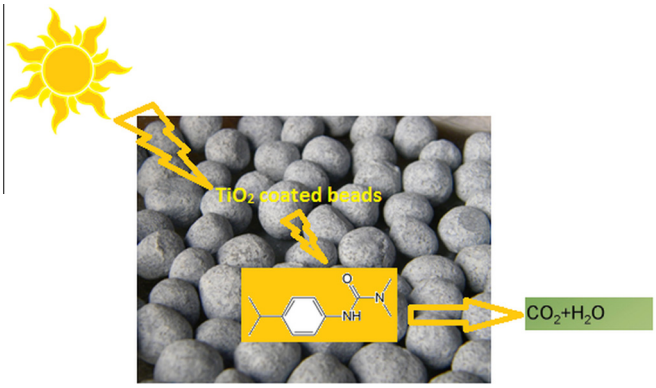
HIGHLIGHTS

- TiO_2 immobilized cement beads were tested for the degradation of isoproturon.
- SEM–EDAX confirms the stability of the coated catalyst even after 30th recycle.
- Solar fixed bed baffled reactor was made using TiO_2 immobilized cement beads for degradation studies.
- LC–MS analysis confirmed the mineralization of isoproturon along with 90% reduction in TOC and COD.

GRAPHICAL ABSTRACT



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Photocatalysis
Mineralization
TiO_2
Herbicide isoproturon

ABSTRACT

The investigation presents the observations on the use of cement beads for the immobilization of TiO_2 for the degradation of herbicide isoproturon. The immobilized system was effective in degrading and mineralizing the herbicide for continuous thirty cycles without losing its durability. Catalyst was characterized by SEM–EDAX for checking the durability of the catalyst. The degradation rate followed first order kinetics as measured by change in absorption intensity in UV range as well as HPLC analysis. Two rounds of TiO_2 coating on inert cement beads with average diameter 1.5 cm at UV Intensity 25 W m^{-2} calcined at 400 °C were the optimized conditions for the degradation of herbicide isoproturon. More than 90% TOC and COD reduction along with ammonium ions generation (80%) confirmed the mineralization of isoproturon. Fixed bed baffled reactor studies under solar irradiations using the TiO_2 immobilized beads confirmed 85% degradation after 6 h. LC–MS studies confirmed the intermediates formation and their subsequent degradation using immobilized system.

1. Introduction

Phenylurea herbicides like isoproturon (IPU) are mainly used for control of annual meadowgrass, blackgrass, ryegrass, silky bentgrass, wild oat, and many broadleaf weeds (Kulshrestha and Muckerjee, 1986; Perrin-Ganier et al., 1996). It is mobile in soil thus easily leached in water bodies (Fomsgaard et al., 2003). Levels above than 0.1 μg L^{-1} are generally detected in water. Its half-life in water and in soils is 30 and 40 d respectively (Perrin-Ganier et al., 1996). It has a high tendency towards bioaccumulation or biomagnification. Exposure to herbicides through any route may cause well-known health effects like acute poisoning, cancer, neurological effects and reproductive and developmental effects

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0045-6535/

(Dhaliwal and Singh, 1993). Incapability of conventional (Meijers et al., 1995; Roche and Prados, 1995; Schuelein et al., 1996) and biological (Sandermann et al., 1998; Parra et al., 2000, 2002a) treatment methods for removal of pesticides has substantially increased the concern. Lack of knowledge, repeated and overdose of pesticides has irreversibly damaged our land, air and water bodies.

A large amount of research has been undertaken in recent past on advanced oxidation processes (AOP) specially heterogeneous photocatalysis for the degradation of toxic compounds (Andreozzi et al., 1999; Haque and Muneer, 2003; Badawy et al., 2006; Dubey et al., 2009; Mohajerani et al., 2009). The mechanism of AOP is now well established which characterizes the formation of hydroxyl radicals (·OH) capable enough to degrade a large variety of bio-recalcitrant organic compounds (Mohajerani et al., 2009). TiO_2 photocatalysis, in slurry form, is gaining more importance in the area of AOP to degrade toxic compounds (Reddy et al., 2011; Verma et al., 2013a) as it is chemically inert, stable, strong oxidizing power and relatively inexpensive. Main technical limitation of this slurry form is basically separation of catalyst from the slurry and huge cost associated behind effective separation. This is one of the major reasons challenging its commercial applications. This problem can be resolved by immobilizing the catalyst on effective support material. Many studies dedicated to TiO_2 immobilization have been reported over different inert supports (Parra et al., 2002b; Daneshvar et al., 2005; Mahmoodi et al., 2006; Sharma et al., 2008a,b). But the durability, cost and recyclability of the immobilized system have not been effectively addressed. Moreover, the inertness of support material is also a major concern, which has not been stressed upon. The present study attempts these pitfalls by selecting spherical beads of cement and sand coated with TiO_2 for the degradation of IPU. The durability is confirmed by recycling the coated beads for thirty times and efficiency is checked by studying the photodegradation of IPU. To best of our knowledge, this is first attempt towards support selection and recycling studies up to at-least thirty times. Effect of operating parameters like number of catalyst coatings, bead diameter, UV intensity, and calcination temperature are also studied for field scale applications. An attempt has also been made to identify the intermediate products through LC–MS analysis along with the mineralization studies.

2. Experimental methods

2.1. Reagents, chemicals and materials

IPU, technical grade (95%), was obtained from Pioneer Pesticides, Chandigarh (India) and used as such without any further purification (Fig. 1). The photo catalyst TiO_2 P-25 (a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30) was used in all heterogeneous experiments and procured from Evonik Industries India, with a BET surface area of 50 $m^2 g^{-1}$ and average particle size of 30 nm. Cement and sand used for making cement beads were procured from local market. Cement beads were made manually and size was selected by making different beads ranging from 1.0 to 2.5 cm. The diameter of bead is taken as average value of the diameter of fifty beads and at different locations. For the preparation of all the solutions double distilled water was used. For pH adjustment, the concentrated solutions of HCl and NaOH (obtained from Merck) were used. Hydrogen Peroxide, H_2O_2 (Ranbaxy, India) was used as an oxidant.

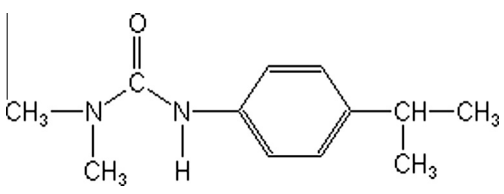

Fig. 1. Chemical structure of isoproturon.

2.2. TiO_2 Immobilization

TiO_2 was coated on cement beads with average diameter ranging from 1.0 to 2.5 cm by dispersing the beads in the TiO_2 slurry until uniform deposition was achieved. To evaporate the excess water, the beads were exposed to 110 °C in lab oven. For the total deposition of the catalyst, beads were further calcined at 400 °C in muffle furnace for 2 h. The same cycle was repeated for two times for getting uniform and stable film of the catalyst. The coated beads were washed with water after each cycle to remove the loosely bound catalyst particles.

2.3. Lab-scale photo reactor set-up and procedure

The photocatalytic experiments with TiO_2 coated cement beads were done in lab scale batch reactor as well as pilot scale reactor. The batch reactor was made up of borosil glass, 16 cm in diameter and 5.2 cm in height with a capacity of 1200 mL. This glass reactor was placed on lab jack in UV chamber (wooden) having dimensions of 1.37 m × 0.9 m × 1.0 m, which had 36 W UV tubes (Philips) attached on the underside of the roof having wavelength of 365 nm for getting required intensity in the chamber (Toor et al., 2007). For the batch photocatalytic experiments, 300 mL solution containing the appropriate amount of immobilized catalyst beads was irradiated for 3–4 h under UV irradiations. At regular intervals, an aliquot of 3 mL was taken from the reaction volume. The sample was filtered using Millipore filter (0.45 μm). The UV intensity was varied by adjusting the height of lab jack from 10 to 24 W m^{-2} corresponding to the average intensity of UV radiation available in sunlight. UV Intensity was measured with an Eppley radiometer (model no.-33013). Aeration was done by purging oxygen at required flow rate from time to time. For proper control of temperature inside the chamber an exhaust was used. All experiments were carried out in triplicate for reproducibility of results.

2.4. Pilot-scale photo reactor set-up

The pilot scale set-up consisted of a baffled reactor 30 cm × 15 cm made up of concrete with four baffles at equal distances. The TiO_2 coated cement beads were placed in each chamber of baffled reactor in such a way that they are effectively submerged in the solution to be treated. The flow rate of the IPU solution was maintained for getting the required retention time. The reactor was covered with transparent sheet for easy penetration of sunlight besides controlling evaporation losses.

2.5. Chemical analysis

The degradation studies were done using UV–Vis spectrophotometer (HITACHI model no. U-2800), with IPU having λ_{max} at 239 nm. The samples were also analyzed using HPLC [Shimazdu, SED-20A] for the confirmation of IPU degradation. HPLC was performed on isocratic HPLC system with C-18 column (250 mm × 4.60 mm), particle size 5 μm using water:acetonitirile (60:40) as mobile system with UV detector at 239 nm for IPU. Flow rate was maintained at 0.5 mL min^{-1}. The degradation products were analyzed by Agilent series LC–MS equipped with an ESI source. The column used was Exclipse XDB C-18 (1.8 um, 4.6 × 150 mm) and the mass spectrum was operated in positive ion mode. The operating conditions are: gas: helium; gas

temperature: 350 °C with flow rate 10 L min^{-1}; nebuliser gas and nitrogen gas pressure: 3102.6 kPa; sheath gas temperature: 320 °C; sheath gas flow rate: 10 L min^{-1}; capillary voltage: 3500 V (positive); nozzle voltage: 0 V; Ionization: positive.

Mineralization studies were performed by measuring ammonium ions (APHA, 1992: Sec. 4550C) generation along with reduction in COD (APHA, 1992: Sec. 5220C) and TOC (Harp, 2002).

3. Results and discussion

3.1. Preliminary studies

Blank experiments were performed using bare cement beads in a UV light using batch reactor. A negligible photodegradation (5%) was observed owing to photolytic activity and adsorption on the bare beads. Moreover, adsorption studies (TiO_2 P-25 only) confirmed 8% reduction in concentration of IPU after 3 h of irradiations (Fig. 2). The loss in concentration is mainly due to the formation of monolayer of the IPU on the catalyst surface. After monolayer formation, no free active sites would be available and therefore no further reduction in concentration was observed (Toor et al., 2007). The use of oxidant (H_2O_2) alone showed 4% degradation due to small amount of OH radicals produced. The combination of all i.e. UV + TiO_2 coated beads + H_2O_2 showed 90% degradation after 5 h of illumination, thus leading to an assumption that adsorption–desorption of the IPU and reaction intermediates are relatively slow as compared to the formation of electron/hole pairs (Haque and Muneer, 2003). In contrary, more than 90% degradation of IPU was achieved in slurry TiO_2 mode after 3 h of irradiations. Although the degradation of IPU is more effective in slurry mode however the separation of catalyst is not feasible.

3.2. Photocatalysis using immobilized cement beads

3.2.1. Effect of number of coatings

The effect of number of TiO_2 coatings on the beads were studied for the photocatalytic degradation studies for IPU. It was observed that the degradation was only 65% if the TiO_2 was coated once over the beads. When the number of coatings of the photocatalyst was increased from 2 to 4 times, the herbicide degradation stabilized after second coating and continued to remain nearly same till 4th coating. Degradation was close to 90% in each of these cases after 5 h of treatment (Fig. 3a). With each cycle of coating, a uniform thickness of TiO_2 film was formed on the surface of cement bead depending upon its size and texture. Beyond a certain thickness of the catalyst, further increase in number of coatings, the catalyst particles are loosely bound and are susceptible to detachment from the immobilized surface. This will additionally obstructs the path of light penetrating the solution leading to the scattering of light by increasing the concentration of TiO_2 in solution along with mass transfer limitations.

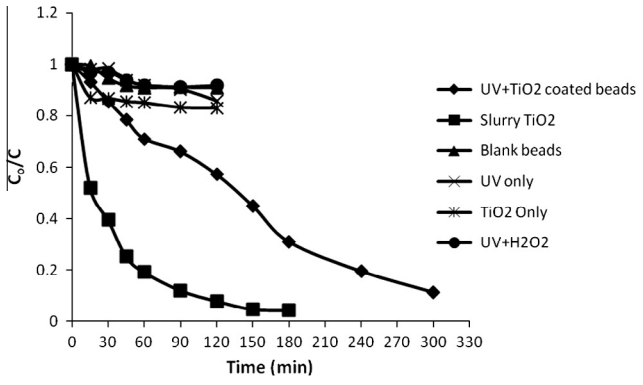

Fig. 2. Photolysis, photocatalytic reduction of isoproturon in the presence and absence of TiO_2 along with adsorption and slurry TiO_2. Experimental conditions: 25 mg L^{-1} isoproturon, V = 300 mL, UV intensity = 23 W m^{-2}.

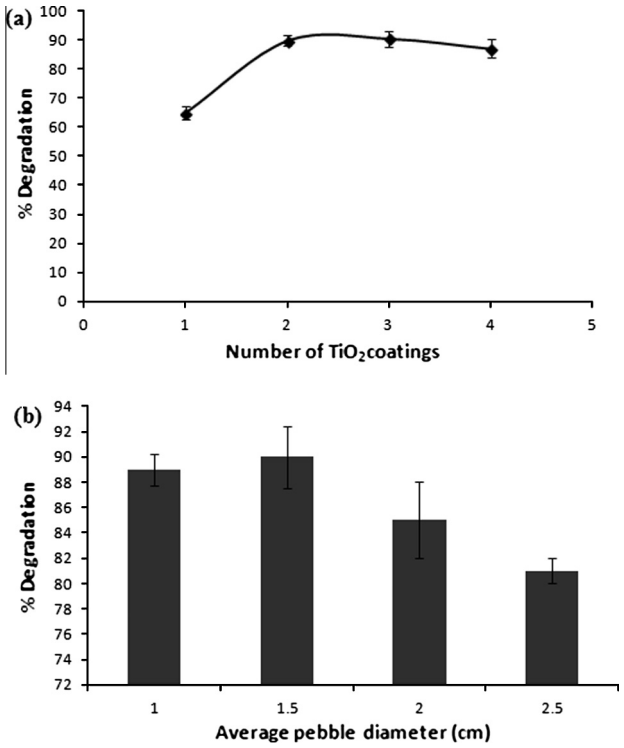

Fig. 3. Percentage degradation data of isoproturon (C_0 = 25 mg L^{-1}) for (a) effect of number of TiO_2 coatings on cement beads (b) varying average diameter of TiO_2 coated cement bead for photocatalytic reduction of Isoproturon.

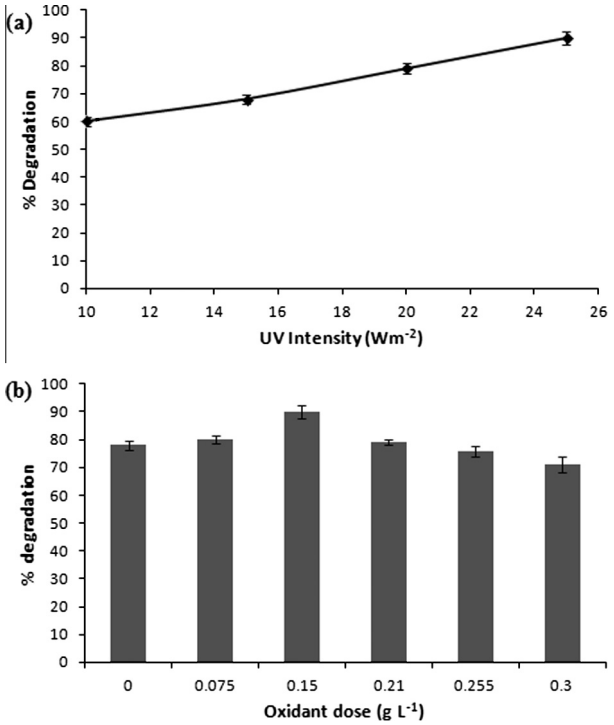

Fig. 4. Plot of percent degradation data versus (a) variation in UV intensity (b) varying H_2O_2 concentration during photocatalytic degradation of isoproturon (C_0 = 25 mg L^{-1}, average bead diameter = 1.5 cm).

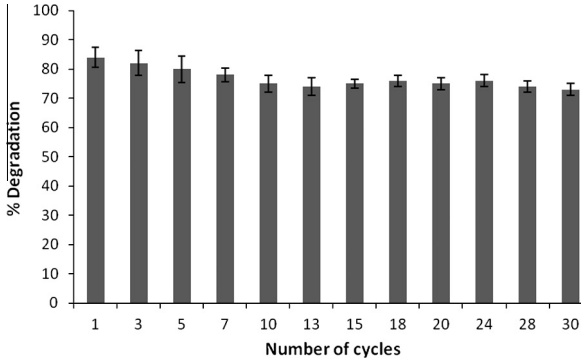

Fig. 5i. Effect of varying H_2O_2 concentration on the photocatalytic degradation of isoproturon (C_0 = 25 mg L^{-1}, UV intensity = 23 W m^{-2}, average bead diameter = 1.5 cm).

3.2.2. Effect of bead/pebble size

In any liquid–solid system, the available surface area for the reaction plays vital and promising factor for its commercial applications. Hence we have studied the degradation of IPU by varying the average surface area of the cement beads. Spherical cement beads were made of different sizes and tested for photocatalytic activity after immobilizing the catalyst. The degradation of IPU decreased from 90% to 80% with the increase in diameter of bead owing to the decrease in effective surface area available (Fig. 3b). The beads with very small diameter 1 cm average, did not yield good degradation which probably was due to catalyst not being effectively immobilized caused by very small surface available for coating.

3.2.3. Effect of UV intensity

For field scale applications of AOP, the UV intensity plays very important. In this view, the intensity of UV radiations was varied from 10 to 25 W m^{-2} in chamber keeping the aperture to volume constant. The degradation of IPU increased from 60% to 90% as the intensity of UV radiation varied from 10 to 25 W m^{-2} (Fig. 4a). With the increase in intensity of light, actual number of OH radicals increases leading to enhancement of degradation rate (Verma et al., 2013b).

3.2.4. Effect of H_2O_2 addition

The role of Hydrogen peroxide for enhancing the photocatalytic degradation rate is now well established. H_2O_2 was varied from 0.25 to 1.0 mL in photodegradation of IPU and addition had synergistic effect as degradation increased to 90% after 4 h of treatment at 0.5 mL optimum dose as shown in Fig. 4b. However overdose of H_2O_2 retards the IPU photocatalytic degradation rates as high concentration of H_2O_2 acts as a scavenger.

3.2.5. Effect of calcination temperature

The cement beads, after the TiO_2 coating, were calcined at different temperatures i.e. 200, 300 and 400 °C for 2 h. The photocatalytic activity of beads calcined at different temperatures was determined by degradation efficiency of IPU. It was evident that the degradation efficiency was better when the beads are calcined at 400 °C than at lower temperature. Further increase in calcination temperature did not enhance the degradation rate as the stability of the coating was also a concern at high temperatures. Heat treatment influences the specific surface of the photocatalyst along with affect on the surface defects and active sites (Shifu and Gengyu, 2005).

3.2.6. Durability studies

The main implication in the studies and applications in fixed-bed catalysis is durability of the supported catalyst. In general, the supported catalyst activity is reported to be reduced after six runs (Parra et al., 2004). The re-activation of the supported catalyst requires high temperatures (480 °C), which is generally not viable from economic point of view. Efforts have been done in present study for checking the durability of the immobilized catalyst on cement beads for the degradation of the IPU. The beads were effectively recycled for at-least thirty times with little reduction in efficiency in context to degradation of IPU (Fig. 5i). To best of our

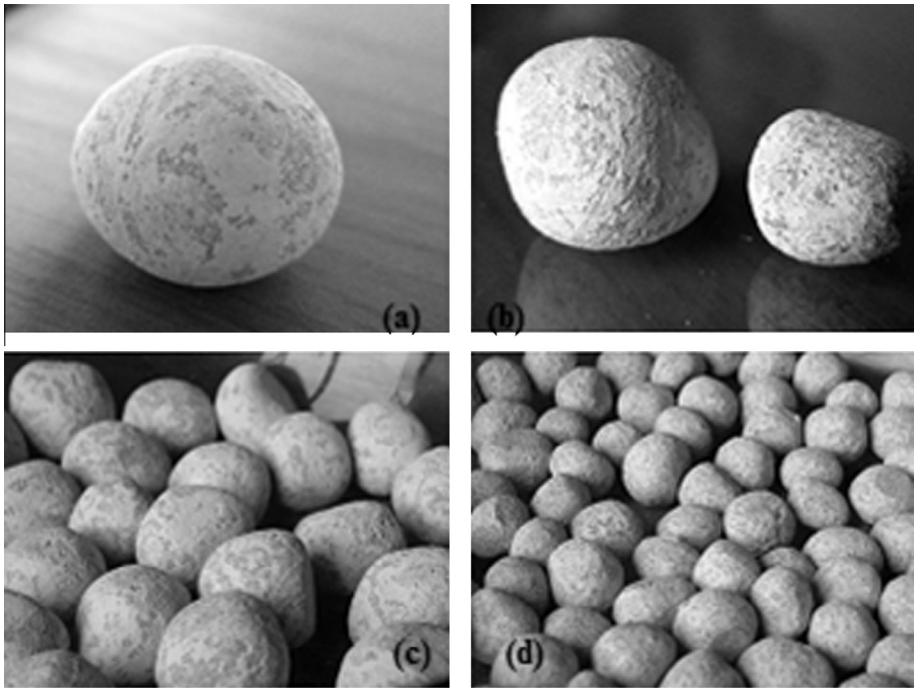

Fig. 5ii. Images of TiO_2 coated cement beads (a) original coating, (b) after 5th recycle, (c) after 15th recycle and (d) after 30th recycle for the degradation of herbicide isoproturon.

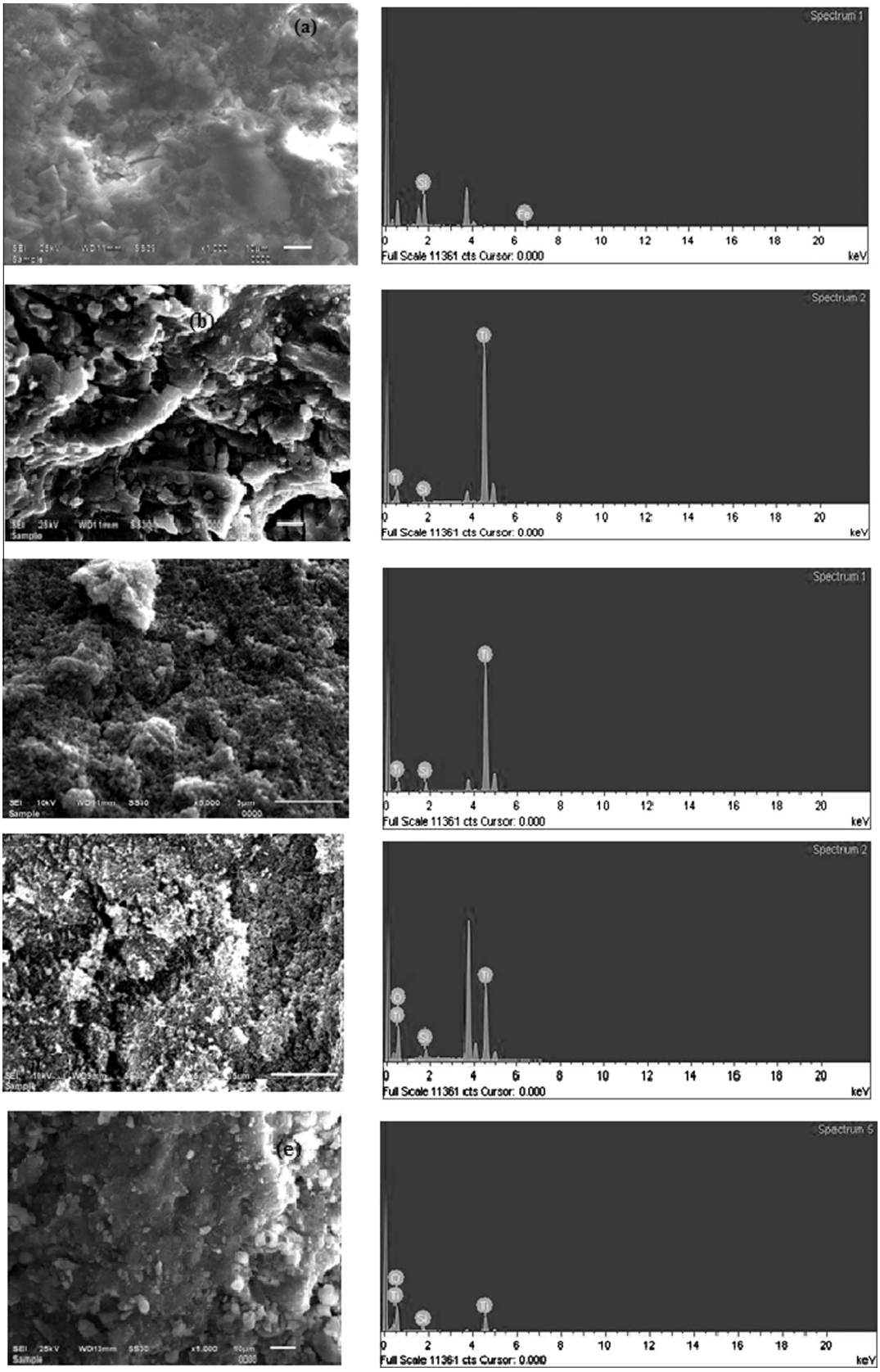

Fig. 5iii. SEM photographs of (a) bare cement beads without TiO_2 coating, (b) fresh coated TiO_2, (c) after 5th recycle, (d) 15th recycle and (e) 30th recycle along with corresponding EDAX measurements.

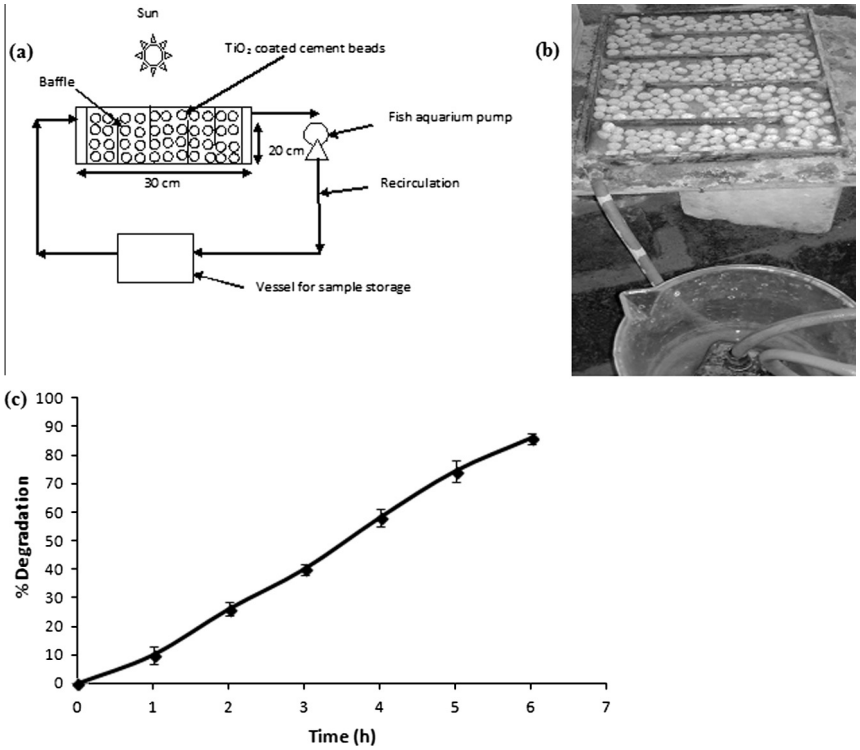

Fig. 6. (a) Fixed bed baffled reactor (FBBR), (b) actual photo of the set-up and (c) degradation of isoproturon under solar irradiations (C_0 = 25 mg L^{-1}, and average solar UV intensity 23 W m^{-2}, average bead diameter = 1.5 cm).

knowledge, this is first reported study of number of recycling (to the extent of thirty times) for the degradation of herbicide IPU or any other compound. Images of the catalyst coated cement beads during various stages of recycling are shown in Fig. 5ii, which show that coating is intact even after 30th cycle, hence can also be further used as such. The morphology of recycled beads was studied using SEM technique and micrograph is presented in Fig. 5iii. From SEM images and EDAX analysis, it is clear that catalyst is intact even after 30th recycle confirming its stability. After each cycle, the catalyst coated cement beads were exposed to solar radiations for 1–2 h otherwise oven heated at 100 °C for one hour for reactivation.

Confirmations were also done by heating the beads in muffle furnace at 400 °C for 1 h and results were crosschecked. No significant change in the percentage degradation of IPU was recorded thus proposing the re-activation at lower temperatures.

3.3. Solar fixed bed baffled reactor studies

An attempt has been made in studying the degradation of IPU in fixed bed baffled reactor (FBBR) under natural sunlight conditions during months of April and May. The average solar and UV intensity was 600 and 28 W m^{-2} respectively (measured from 10.00 AM to 4.00 PM) with surrounding temperature 30 ± 4 °C. The FBBR (30 cm × 20 cm) was made of sand and cement with four baffles placed at equal distances (Fig. 6a and b). The cement beads coated with TiO_2 (method described above) were used in proportion to area calculations to that of lab scale reactor. The depth of the FBBR was sufficient enough to submerge the catalyst coated beads. The FBBR was operated in recirculation mode with flow rate maintained at 0.5–1.0 L min^{-1}. The 85% degradation of IPU was observed after 6 h of treatment (Fig. 6c). Recycling studies were also performed for FBBR, where the same set-up was used for another twenty batches for studying degradation of IPU. Attrition is basically main problem observed in flow systems but in our case, there is negligible attrition as confirmed from constant degradation data. Actually treatment time can be reduced by increasing the retention time of solution in FBBR, which requires design modifications of the reactor. With these modifications, along with studied immobilized surface, reactor can boost the commercial applications of fixed bed photocatalysis.

3.4. Mineralization studies

The mineralization studies of IPU have been carried out in terms of TOC reduction along with NH_4^+ generation. In our study, we have achieved 92% reduction in COD and 90% reduction in TOC after 5 h of photo-treatment of IPU during which release of ammonium ions was maximum. Under optimized conditions, the release of NH_4^+ ions reached 65% during first 2 h of treatment and subsequently reached to constant value of 80% after 5 h of treatment. The LC–MS analysis of the treated sample confirmed the formation of various intermediates viz. (i) monodemethylisoproturon (ii) didemethylisoproturon (iii) 3-hydroxy isoproturon during photocatalytic degradation of isoproturon, as reported in our previous studies (Verma et al., 2013c; Refer to Supplemental Material (SM) for byproducts).

4. Conclusion

The present study attempts immobilization of TiO_2 on cement beads for the degradation of herbicide IPU. The effect of number of coatings as well as bead diameter has been studied for the first time along with its durability studies. The parameters like oxidant concentration (H_2O_2), UV intensity, effect of calcination temperature play important role affecting the photocatalytic degradation rate, thus deciding the optimized conditions. Two coatings of TiO_2 on cement beads of 1.5 cm diameter calcined at 400 °C proved

best optimum conditions for the degradation of IPU. The COD reduction (92%) along with ammonium ion generation (80%) confirmed the mineralization of the herbicide, IPU. From SEM and EDAX analysis, catalyst stability is proved even after 30th recycle, thus confirms its applications for several cycles for the degradation of herbicides without losing its original activity. Intermediates formed gradually disappeared during photocatalytic treatment of IPU as confirmed from HPLC and LC–MS data.

Acknowledgements

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Appendix A. Supplementary material

LC–MS data for the degradation of IPU is provided as supplementary data. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.02.051.

References

Andreozzi, R., Caprio, V., Insola, A., Marotta, R., 1999. Advanced oxidation processes (AOP) for water purification and recovery. Catal. Today 53, 51–59.

APHA, 1992. Standard Methods for the Examination of Water and Wastewater, 19, 18th eds. American Public Health Association, Washington, DC.

Badawy, M.I., Montaser, Y.G., Tarek, A., 2006. Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater. Desalination 194, 166–175.

Daneshvar, N., Salari, D., Niaei, A., Rasoulifard, M.H., Khataee, A.R., 2005. Immobilization of TiO_2 nanopowder on glass beads for the photocatalytic decolorization of an azo dye C.I. Direct Red 23. J. Environ. Sci. Health, Part A 40, 1605–1617.

Dhaliwal, G.S., Singh, B. (Eds.), 1993. Pesticides: Their Ecological Impact in Developing Countries. Commonwealth Publishers, New Delhi.

Dubey, S.K., Kumar, A., Srivastava, P., Anita, R., 2009. Solar photo-catalytic treatment of textile wastewater for biodegradability enhancement. J. Environ. Eng., 152–164.

Fomsgaard, I.S., Spliid, N.H., Felding, G., 2003. Leaching of pesticides through normal-tillage and low-tillage soil – a lysimeter study. I. Isoproturon. J. Environ. Sci. Health, Part B 38, 1–18.

Haque, M.M., Muneer, M., 2003. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspensions of titanium dioxide. J. Environ. Manage. 69, 169–176.

Harp, D.L., 2002. Total Organic Carbon (Direct method). U.S. Patent 6,368,870, April 09.

Kulshrestha, G., Muckerjee, S.K., 1986. The photochemical decomposition of the herbicide isoproturon. Pestic. Sci. 17, 289–494.

Mahmoodi, N.M., Arami, M., Limaeei, N.Y., 2006. Photocatalytic degradation of triazinic ring-containing azo dye (reactive red 198) by using immobilized TiO_2 photoreactor: Bench scale study. J. Hazard. Mater. B 133, 113–118.

Meijers, R.T., Oderwald-Muller, E.J., Nuhn, P.A.N.M., Kruithof, J.C., 1995. Degradation of pesticides by ozonation and advanced oxidation. Ozone Sci. Eng. 17, 673–686.

Mohajerani, M., Mehrvar, M., Ein-Mozaffari, F., 2009. An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment. Int. J. Eng. Sci. 3, 120–127.

Parra, S., Sarria, V., Malato, S., Peringer, P., Pulgarin, C., 2000. Photochemical versus coupled photochemical–biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon. Appl. Catal., B 27, 153–168.

Parra, S., Olivero, J., Pulgarin, C., 2002a. Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO_2 suspensions. Appl. Catal., B 36, 75–85.

Parra, S., Malato, S., Pulgarin, C., 2002b. New Integrated photocatalytic-biological flow system using supported TiO_2 and fixed bacteria for the mineralization of isoproturon. Appl. Catal., B 36, 131–144.

Parra, S., Stanca, S.E., Guasaquillo, I., Thampi, K.R., 2004. Photocatalytic degradation of atrazine using suspended and supported TiO_2. Appl. Catal., B 51, 107–116.

Perrin-Ganier, C., Breuzin, C., Portal, J.M., Schiavon, M., 1996. Availability and persistence of isoproturon under field and laboratory conditions. Ecotoxicol. Environ. Saf. 35, 226–230.

Reddy, P.A.K., Srinivas, B., Kala, P., Kumari, V.D., Subrahmanyam, M., 2011. Preparation and characterization of Bi-doped TiO_2 and its solar photocatalytic activity for the degradation of isoproturon herbicide. Mater. Res. Bull. 46, 1766–1771.

Roche, P., Prados, M., 1995. Removal of pesticides by use of ozone or hydrogen peroxide/ozone. Ozone Sci. Eng. 17, 657–672.

Sandermann, H., Heller, W., Hertkorn, N., Hoque, E., Pieper, D., Winkler, R., 1998. A new intermediate in the mineralization of 3,4-dichloroaniline by the white rot fungus *Phanerochaete chrysosporium*. Appl. Environ. Microbiol. 64, 3305–3312.

Schuelein, J., Glaessgen, W.E., Hertkorn, N., Schroeder, P., Sandermann, H., Kettrup, A., 1996. Detection and identification of the herbicide isoproturon and its metabolites in field samples after a heavy rainfall event. Int. J. Environ. Anal. Chem. 65, 193–202.

Sharma, M.V.P., Kumari, V.D., Subrahmanyam, M., 2008a. Photocatalytic degradation of isoproturon herbicide over TiO_2/Al-MCM-41 composite systems using solar light. Chemosphere 72, 644–665.

Sharma, M.V.P., Kumari, V.D., Subrahmanyam, M., 2008b. TiO_2 supported over SBA-15: an efficient photocatalyst for the pesticide degradation using solar light. Chemosphere 73, 1562–1569.

Shifu, C., Gengyu, C., 2005. Photocatalytic degradation of organophosphorus pesticides using floating photocatalyst TiO_2·SiO_2/beads by sunlight. Solar Energy 79, 1–9.

Toor, A.P., Verma, A., Singh, V., Jotshi, C.K., Bajpai, P.K., 2007. Treatment of bleaching effluents from the pulp and paper industry by photocatalytic oxidation. Tappi J. 6, 9–13.

Verma, A., Kaur, H., Dixit, D., 2013a. Photocatalytic, sonolytic and sonophotocatalytic degradation of 4-chloro-2-nitro phenol. Arch. Environ. Prot. 39, 65–76.

Verma, A., Sheorn, M., Toor, A.P., 2013b. Titanium dioxide mediated photocatalytic degradation of malathion in aqueous phase. Indian J. Chem. Technol. 20, 46–51.

Verma, A., Prakash, N.T., Toor, A.P., 2013c. Photocatalytic degradation of herbicide isoproturon in TiO_2 aqueous suspensions: study of reaction intermediates and degradation pathways. Environ. Prog. Sustain. Energy. http://dx.doi.org/10.1002/ep.11799.

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Photocatalytic Degradation of Herbicide Isoproturon in TiO_2 Aqueous Suspensions: Study of Reaction Intermediates and Degradation Pathways

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Heterogeneous photocatalytic degradation and mineralization of Isoproturon (IPU) was investigated in aqueous solutions containing titanium dioxide. The degradation was monitored by observing the change in absorption intensity in UV range and through HPLC analysis. The degradation rate was found to be strongly dependent on catalyst concentration, initial pH, and substrate concentration. The effect of variation in intensity of UV irradiations, catalyst recycling as well as area/volume is also studied for the practical applications. The degradation rate was observed to follow first-order kinetics. TiO_2 loading 0.5 g L^{-1}, pH 5.0, C_0 = 25 mg L^{-1} were the optimized conditions for obtaining the better degradation rates. Reduction in COD and TOC values along with the generation of ammonium further indicated the mineralization of the IPU. Fixed bed studies on glass sheet and small cement slabs eliminates the drawbacks of slurry mode photocatalysis. An attempt was also made to identify the intermediates (degradation products) through LC-MS analysis. © *2013 American Institute of Chemical Engineers Environ Prog, 00: 000–000, 2013*

Keywords: photocatalysis; degradation; COD; TOC; mineralization; TiO_2; isoproturon

INTRODUCTION

Herbicide pollution of surface water and groundwater has been recognized as a major problem in many developing countries because of the persistence of pollutants in aquatic environments [1,2]. One of the consequences of indiscriminate use of herbicide is the adverse health impact on society in general and vulnerable population like children in particular. Humans are exposed to herbicides found in environmental media (soil, water, air, and food) by different routes of exposure such as inhalation, ingestion, and dermal contact. Some of the well-known health effects of herbicide exposure include acute poisoning, cancer, neurological effects, and reproductive and developmental effects [3]. The lack of any effective treatment of water containing herbicides has invited many researchers for novel treatment options.

The use of advanced oxidation processes (AOPs) such as heterogeneous as well as homogeneous photocatalysis have been the widely studied in the past for the degradation of pesticides and herbicides [4–8]. These advanced processes are attractive treatment options as they completely degrade the herbicides without transferring them in other phases unlike other treatments like adsorption and air stripping [9]. TiO_2, now widely accepted photocatalyst, is inexpensive, stable, and inert. The mechanism of the heterogeneous photooxidation and reduction is well established and discussed extensively in the literature. Hydroxyl radicals ($^{\bullet}OH$) generated are nonselective in nature and they can react without any other additives with a wide range of contaminants whose rate constants are usually in the order of 10^6–10^9 mol L^{-1} s^{-1}. These •OH radicals attack organic molecules resulting in new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization [10].

The model compound, isoproturon (IPU), is mainly used for control of annual meadowgrass, blackgrass, ryegrass, silky bentgrass, wild oat, and many broadleaf weeds. This herbicide enters the environment during its application in agricultural fields, but may also be found during manufacture, transportation, and storage. IPU has a low tendency to adsorb to soils and is therefore easily released into aqueous environments. Levels above than 0.1 μg L^{-1} are generally detected in water. Its half-life in water and in soils is 30 and 40 days, respectively [11,12]. Due to its low affinity for organic matter, it is not expected to have a high tendency toward bioaccumulation or biomagnification.

To handle the heavy pollutant load in commercial applications, the catalyst amount should be minimum to support the economics of the treatment process. Moreover, the design as well as maintenance of reactors studied in literature [13–15] is very challenging as far as technical applications of this technology are concerned. Shallow pond reactors with recirculation mode are very effective in treating large quantity of waste with both slurry and fixed bed. For this kind of application, the depth of the pond reactor, effect of UV intensity, effective material for catalyst immobilization as well as catalyst recycling are the major parameters to be studied upon. Studies have been reported earlier in context to degradation of IPU using heterogeneous photocatalysis in slurry form [16], fixed mode [17], coupled photocatalytic-biological flow reactor system [18], and identification of

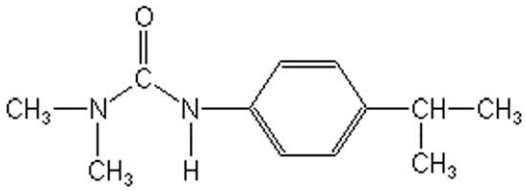


Figure 1. Chemical structure of Isoproturon.

various intermediates [19]. But considerable gaps are there in context to above cited literature like catalyst loading is always on higher side, that is, 1.0−1.5 g L^{-1}; effect of operating parameters for field scale applications like area/volume (A/V), UV intensity, effective immobilized surface, catalyst recycling, etc. are not effectively touched. In addition, there is limited information on the intermediates or degradation products forming during the photocatalytic activity.

These parameters are not effectively addressed in the literature to the best of our knowledge creating gap between laboratory and commercial applications. This study attempts some of these shortfalls for the photodegradation of IPU (Figure 1) in slurry form. Detailed study have been undertaken to study the effect of various operating parameters like pH, substrate, and catalyst concentration along with variation in intensity of UV irradiations as well as A/V is also studied for the practical applications. An attempt has been made to identify the intermediate products through LC-MS analysis along with the mineralization studies. Fixed bed catalysis has also been studied using inert supporting materials keeping commercial applications in mind.

MATERIALS AND METHODS

IPU, N,N-dimethyl-N′-[4-(1-methylethyl)phenyl] urea, Technical grade (95%), structure of which is shown in Figure 1, was obtained from Pioneer Pesticides, Chandigarh (India) and used as such without any further purification. For the preparation of all the solutions double distilled water was used. The photocatalyst TiO_2 P-25 (a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30) was used in all heterogeneous experiments and procured from Evonik Industries India, with a BET surface area of 50 m^2 g^{-1} and average particle size of 30 nm. For pH adjustment the concentrated solutions of HCl and NaOH (obtained from Merck) were used. Hydrogen Peroxide, H_2O_2 (Ranbaxy, India) was used as an oxidant.

Experimental Setup

For the experiments under UV light, the chamber used was rectangular in shape having dimensions of 4.5 × 3.0 × 3.5 ft^3 and made up of galvanised iron sheet. Seven 36 W UV tubes (Philips) were attached in parallel on the underside of the roof having wavelength of 365 nm. The batch reactor made up of borosil glass, 16 cm in diameter and 5.2 cm in height with a capacity of 1200 mL, was placed on a laboratory jack so that required intensity could be attained by adjusting the distance of the reactor from the UV tubes [20]. The average UV intensity can be varied from 10 to 24 W m^{-2} corresponding to the average intensity of UV radiation in sunlight. UV Intensity was measured with an Eppley (model no.-33013) radiometer. An exhaust fan was employed for proper control of temperature inside the chamber.

Photocatalyst Immobilization

A glass sheet 18 × 10 cm^2 was roughened with sand paper, washed with 10% nitric acid, and subsequently dried. The appropriate amount of catalyst was taken according to area calculation in slurry batch reactor (0.5 g L^{-1}). Catalyst slurry was made in double distilled water and sonicated for

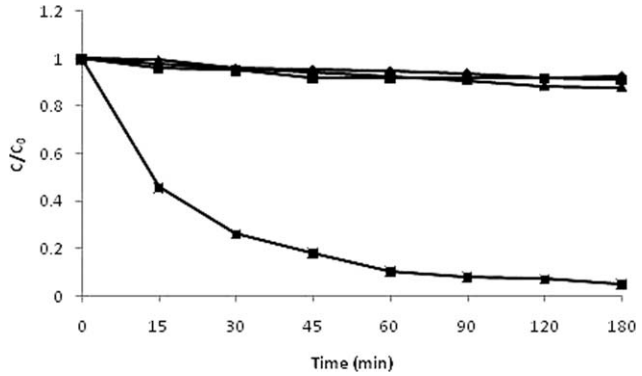


Figure 2. Comparison between photolysis and photocatalytic reduction of Isoproturon in the presence and absence of TiO_2 along with adsorption studies (■ → UV + TiO_2, ▲ → TiO_2, ■ → UV + H_2O_2, ◆ → UV). Experimental conditions: 25 mg L^{-1} isoproturon, V = 200 mL, and UV intensity = 23 W m^{-2}.

1 h for the uniform dispersion of the catalyst. The catalyst was coated on the plate following protocol similar to dip and coating method [21]. In brief, based on the concentration of the catalyst required per unit area, slurry was prepared and sonicated. This slurry was then coated on the glass sheet in the form of film. The coated plate was left in oven at 110°C for overnight and washed in morning to remove loosely coated particles. The method was repeated twice for getting the uniform thickness of the catalyst. Similar method was adopted for the immobilization of the photocatalyst on the small cement slabs (3 × 3 cm^2) made in laboratory.

Procedure

The stock solution of IPU (50 mg L^{-1}) was prepared by dissolving technical grade herbicide in double distilled water and kept for overnight stirring. To achieve the complete adsorption equilibrium, the solution containing the catalyst was maintained in the dark for at least 1 h. For the batch photocatalytic experiments, 200 mL solution containing the appropriate amount of catalyst was irradiated for 4–5 h under UV. The aeration was provided using ambient air with flow rate of 4.5 L h^{-1}. An aliquot of 3 mL was taken from the reaction volume of 200 mL at regular intervals. The sample was filtered using Millipore filter (0.45 mm). The process was optimized by varying the parameters like catalyst dose, pH, UV intensity based on which reaction kinetics was studied. These optimized conditions were used for the further treatment of the samples containing Isoproturon. All experiments were carried out in triplicate for reproducibility of results.

The photocatalytic degradation rates of various organic compounds over TiO_2 can usually be described by a pseudo-first order kinetic expression, that is,

$$-dC/dt = kC \quad \text{or} \quad \ln \quad C_0/C = kt \tag{1}$$

A plot of ln C_0/C versus time represents a straight line and slope of which gives k, an apparent first-order reaction rate constant. C_0 and C are initial and final concentration of the reactant, respectively. In our studies, the degradation rate of the Isoproturon was calculated from the initial slope obtained from the linear plot of natural logarithm of change in concentration of the Isoproturon as a function of irradiation time. From these plots, corresponding value of first order rate constant was calculated and subsequently used in kinetic studies.

Analytical Methods

Degradation of isoproturon was confirmed using HPLC [Shimazdu, SED-20A]. After regular interval of time, small

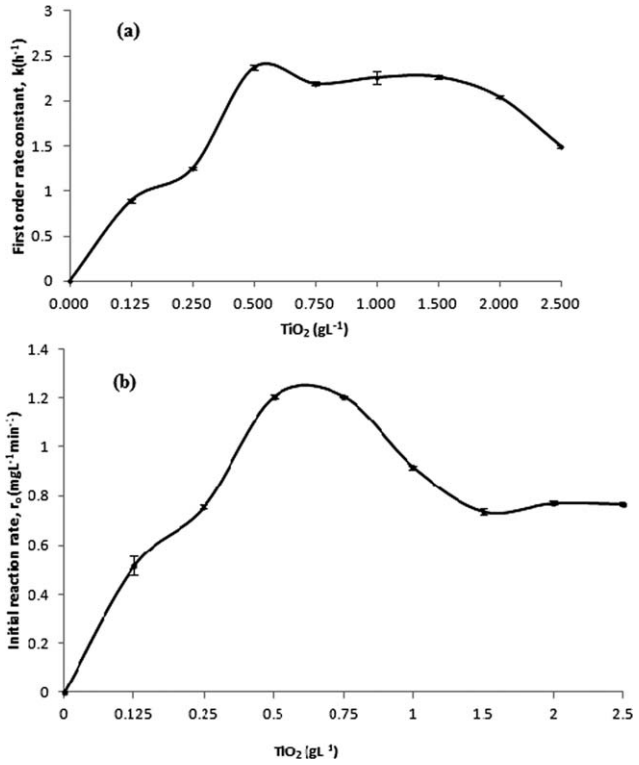


Figure 3. Plot of first order rate constant (a) and initial reaction rate (b) vs. TiO_2 concentration for photocatalytic degradation of isoproturon (reaction volume = 200 mL, TiO_2 = 0.5 g L^{-1}, C_0 = 25 mg L^{-1}, and UV intensity 23 W m^{-2}).

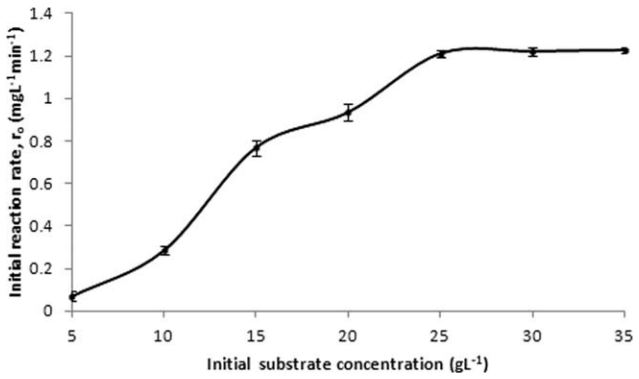


Figure 4. Effect of isoproturon concentration on the initial photodegradation rate during photocatalytic degradation (reaction volume = 200 mL, TiO_2 = 0.5 g L^{-1}, pH = 5.0, and UV intensity 23 W m^{-2}).

aliquot was withdrawn and analysed using HPLC. HPLC was performed on isocratic HPLC system with C-18 column (250 × 4.60 mm^2), particle size-5 μm using water:acetonitirile (60:40) as mobile system with UV detector at 239 nm for isoproturon. Flow rate was maintained at 0.5 mL/min. The λ_{max} for isoproturon was found at 239 nm on a UV–vis spectrophotometer (HITACHI model no. U-2800) and accordingly the degradation studies were done on this λ_{max}. The intermediate products were analyzed by Agilent series LC-MS equipped with an ESI source. The column used was Exclipse XDB C-18 (1.8 μm, 4.6 × 150 mm) and the mass spectrum was operated in positive ion mode. The operating conditions

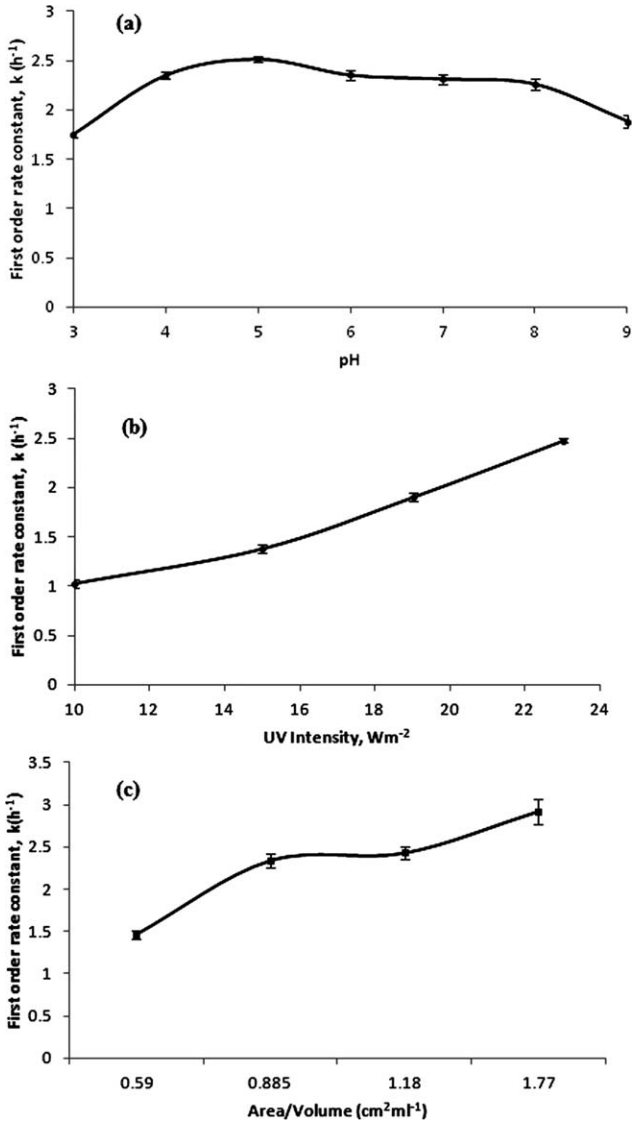


Figure 5. Plot of first order rate constant vs. variation in pH (a), variation in UV intensity (b) and effect of A/V ratio (c) during photocatalytic degradation of isoproturon (TiO_2 = 0.5 g L^{-1}, C_0 = 25 mg L^{-1}).

are as follows: gas: Helium; gas temperature: 350°C with flow rate 10 L min^{-1}; nebulizer gas and nitrogen gas pressure: 450 psi; sheath gas temperature: 320°C; sheath gas flow rate: 10 L min^{-1}; capillary voltage: 3500 V (positive); nozzle voltage: 0 V; ionization: positive.

For the mineralization studies, reduction in COD, generation of ammonium ions as well as depletion in total organic carbon (TOC) were carried out. Standard methods were used for calculating TOC [22], NH_4^+ [23], and COD [24].

RESULTS AND DISCUSSION

Photolytic and Adsorption Studies

The photolytic treatment of the Isoproturon aqueous solution was studied in the batch reactor. The study confirmed negligible photodegradation (6%) of the compound thus describing that the degradation observed in the presence of catalyst is due to catalyst activity (Figure 2). The loss of the Isoproturon in blank, due to adsorption on the surface of the TiO_2 P-25 in dark, was observably negligible (8%) after 180

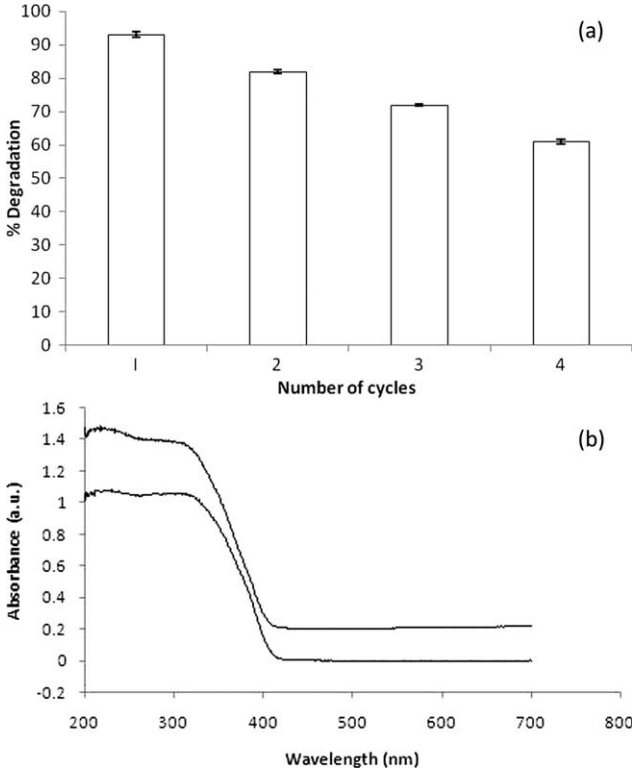


Figure 6. (a) Catalyst recycling studies for the slurry mode during photocatalytic degradation of isoproturon. (b) UV–vis DRS spectra of (a) Fresh TiO_2 (b) recycled TiO_2 after fourth cycle for the degradation of isoproturon under UV irradiations (C_0 = 25 mg L^{-1}, pH = 5.0, and UV intensity 23 W m^{-2}).

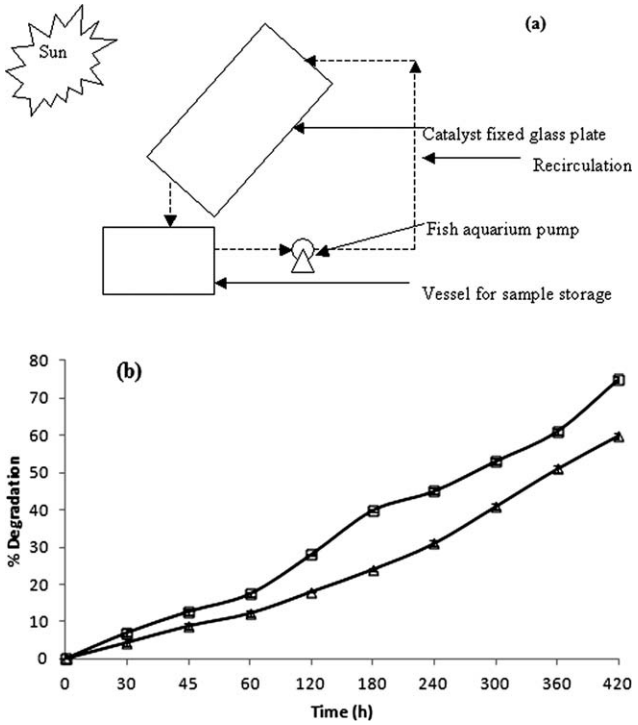


Figure 7. (a) Schematic diagram for fixed bed photocatalysis. (b) Fixed bed photocatalysis (i) □ = glass sheet and (ii) Δ = cement slab for the degradation of isoproturon under UV irradiations (C_0 = 25 mg L^{-1}, pH = 5.0, and Solar UV intensity 23 W m^{-2}).

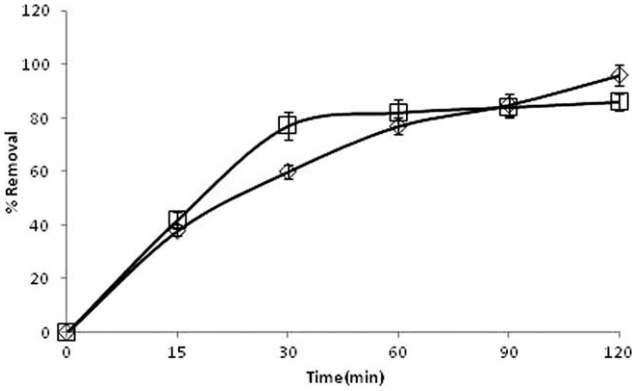


Figure 8. COD reduction (□) and ammonium ion (◇) generation during the photocatalytic degradation of isoproturon.

min of irradiations. The loss in concentration is mainly due to the formation of monolayer of the Isoproturon on the catalyst surface. After monolayer formation, no free active sites would be available and therefore no further reduction in concentration was observed [25]. The photocatalytic treatment showed 95% degradation, thus leading to an assumption that adsorption-desorption of the Isoproturon and reaction intermediates are relatively slow as compared with the formation of electron/hole pairs [7]. A similar study has been carried out for the photolysis of the Isoproturon under UV light [16].

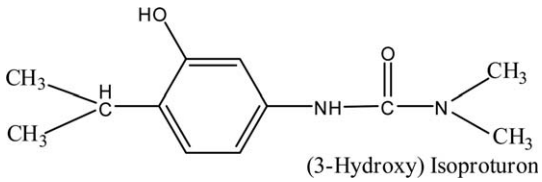
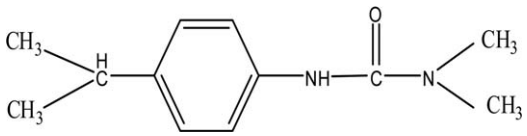
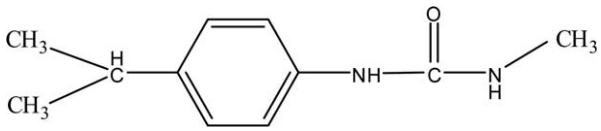
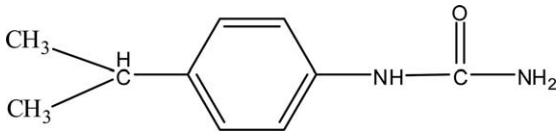
Effect of Photocatalyst Concentration

The effect of photocatalyst concentration on the degradation kinetics of the isoproturon was studied by varying the TiO_2 concentration from 0.125 to 2.5 g L^{-1}. Figure 3a shows a plot of the first-order rate constant (k) as well as initial reaction rate (Figure 3b) as a function of the catalyst concentration. It is observed that as catalyst concentration varied from 0.125 to 0.5 g L^{-1}, there was an increase in photocatalytic activity followed by decrease after 0.5 g L^{-1}. Initially, increase in the rate owes to the increase in the number of photons absorbed in UV light with large number of catalyst particles. Above a certain concentration of catalyst, aggregation of TiO_2 takes place causing a decrease in the number of active sites on its free surface leading to reduction in surface area and thus photocatalytic rate. In addition, the higher concentration of the catalyst obstructs the path of light penetrating the solution leading to the scattering of light [20]. All these factors lead to the reduction of OH radicals owing to decrease in the rate of photocatalytic reaction. A similar kind of effect was studied in the case of photocatalytic degradation of acephate using TiO_2 catalyst using artificial ultraviolet light [26]. However, the optimized catalyst dose (0.5 g L^{-1}) in this study is significantly lower than the one reported [27] for degradation of isoproturon.

Effect of Initial Substrate Concentration

To study the effect of substrate concentration on the degradation rate, the isoproturon concentration was varied from 5 to 30 mg L^{-1} with 0.5 g L^{-1} TiO_2. Initial reaction rate (r_o) increased with increasing concentration of the isoproturon from 5 to 25 mg L^{-1} then becomes constant as shown in Figure 4. As the photocatalytic degradation proceeds with the Langmuir-Hinshelwood (L-H) law, that is, the rate is first

Table 1. Mass spectra data for study of intermediates during photocatalytic degradation of isoproturon by LC-MS.

S. No.	Compound name	t_r (min)	*m/z* ratios of main MS/MS fragments
1.	 (3-Hydroxy) Isoproturon	6.23	223, 205, 181, 165, 73
2.	Isoproturon 	8.12	207,165, 134
3.	Monodemethylisoproturon 	7.51	193,151, 136
4.	Didemethylisoproturon 	6.95	179,162, 144, 134, 119

order at lower substrate concentration and becomes zero order at higher concentrations [25]. Similar trend has been observed in our studies as degradation rate becomes constant after 25 mg L^{-1}. The other reason may be due to insufficient production of OH radicals by the catalyst for the higher concentration of the substrate. Sufficient data is available in literature suggesting the equilibrium between adsorption of the substrate molecules on the catalyst surface and the generation of the OH radicals from the active sites [28].

Effect of pH

The effect of initial pH on the photocatalytic degradation of isoproturon is presented in Figure 5a with the optimum amount of catalyst 0.5 g L^{-1}. The pH of the solution plays an important role in photocatalytic reactions taking place on the semiconductor's surface. Initial pH of the solution depicts the surface charge properties of the catalyst and thus the adsorption of the compound. The point of zero charge (pzc) of the TiO_2 (Degussa P-25) is widely reported at pH = 6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution [20]. In our case, the degradation rate was slightly higher in acidic pH and decreased gradually towards basic pH.

Effect of UV Intensity

For the practical application of AOP in the field, the utilization of sunlight is always preferred. The intensity of solar UV radiations varies throughout the year [29]. Hence, the aqueous solution of isoproturon containing optimum amount of TiO_2 was exposed to different intensity of UV radiations keeping the aperture to volume (A/V) constant. The degradation rate constant increases from 1.026 to 2.478 h^{-1} as the intensity varies from 10 to 23 W m^{-2}, respectively. Actually, with the increase in UV intensity, more number of OH radicals are produced as more radiations fall on the catalyst leading to high rate of degradation (Figure 5b).

Effect of A/V Ratio of the Batch Reactor

The depth of the solution is very critical for deciding the reactor configuration in commercial applications. Generally, less depth and more area is recommended so that light (UV or solar) can penetrate effectively in solution to be treated [30]. In this study, the A/V of the shallow pond reactor was varied from 0.59 to 1.77 cm^2 mL^{-1}. The photocatalytic degradation rate increased with increase in aperture to volume ratio of the reactor. With more A/V ratio, surface area of the solution is enhanced leading to increase in path length of photons entering the solution resulting in higher OH radical yield. Surface area can be increased by keeping the volume constant and increasing the aperture or by keeping the aperture constant and decreasing the volume. In our study, we have kept the aperture constant and varied the volume of the solution (Figure 5c).

Catalyst Recycling

For the industrial applications of photocatalytic process in slurry mode, the recycling of the photocatalyst is very important component to reduce the cost implications. Actually catalyst lifetime is very important for deciding the cost concerns of the catalyst. To understand this, catalyst recycling studies have been done and presented in Figure 6a. After each cycle, the photocatalyst was filtered using Wattmann filter paper (no. 22) and oven dried at 85°C before being used again. In our case, the photocatalyst was recycled effectively for four times but with 12%

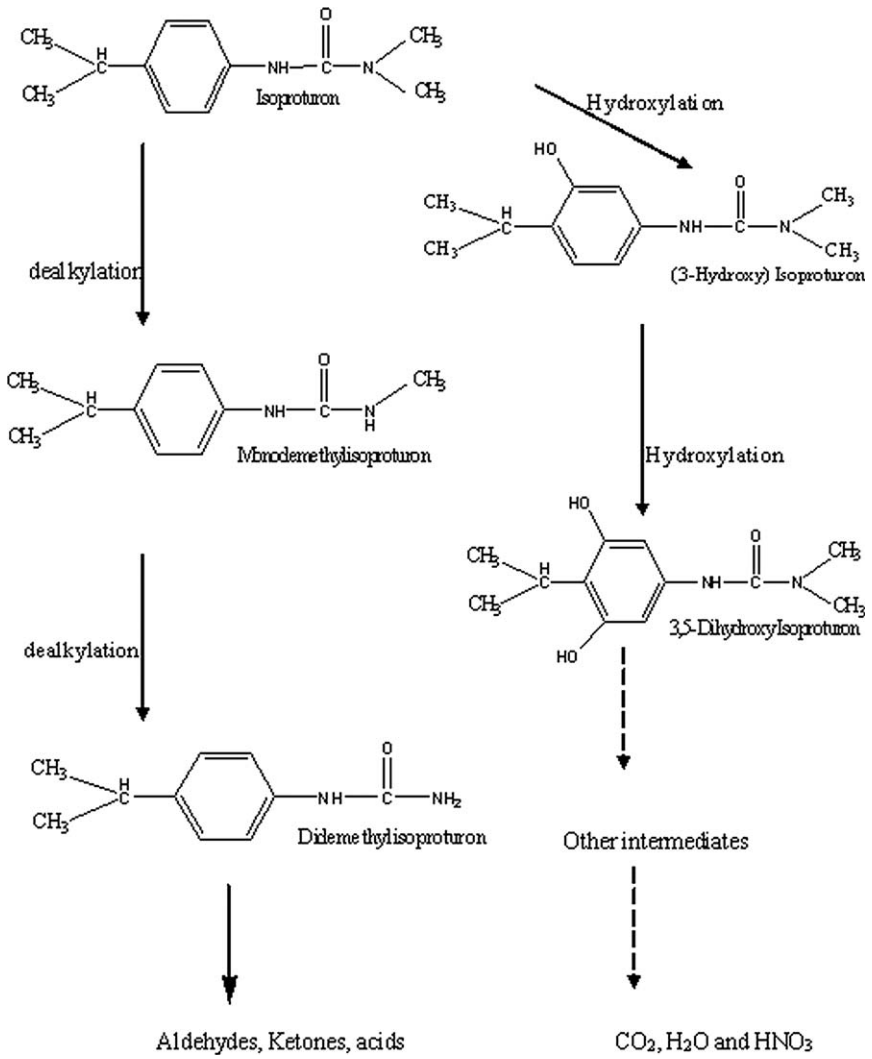


Figure 9. Tentative pathway for photocatalytic degradation of isoproturon [35].

reduction in the efficiency. The UV–vis DRS spectra confirmed that band gap as well as wavelength excitations are not changed for fresh and used catalyst (Figure 6b). The major reason behind the reduction in the degradation rate is catalyst fouling due to accumulation of the pollutant on the surface of the catalyst [31]. The loss of small amount of catalyst during filtration can also be accounted for efficiency reduction.

Fixed Bed Studies

With the view of commercial applications, an attempt was made for immobilizing the catalyst on the inert supports. With the method described above, the immobilized reactor was operated in natural sunlight conditions in recirculation mode with minimum loss of catalyst (Figure 7a). The slope of reactor was adjusted to maintain the flow rate of isoproturon for maximum degradation. The degradation achieved was nearly 70% in case of glass coated reactor and 55% in case of immobilization on cement slabs (Figure 7b). The degradation of Isoproturon was obviously less than the slurry mode due to the diffusional limitations of the substrate, but the immobilized surface was recycled for at-least 10 times with negligible reduction in efficiency. With little modifications, the surface as well as reactor can be modified to boost the commercial applications of fixed bed photocatalysis.

Mineralization Studies

Generally complete photodegradation of the organic compound leads to the formation of CO_2 and various inorganic anions and cations [32]. In our study, the extent of mineralization was studied in terms of COD reduction along with the ammonium ions generation. The 96% reduction COD of the isoproturon was observed after 2 h of irradiation during, which release of ammonium ions was maximum. Further, the initial (16 mg L^{-1}) and final (1.6 mg L^{-1}) TOC measurements, under the optimized conditions, indicated a reduction by 90%. The monitoring of ammonium ions showed a rapid increase in initial 30 min of irradiation (77%) reaching a constant value (88%) after 2 h of photocatalytic treatment under optimized conditions as depicted in Figure 8. The spectra confirmed the diminishing of parent compound peaks along with the generation of some intermediates. The LC-MS analysis showed the presence of major intermediate product as monodemethylisoproturon (product 3) during the course of reaction (Table 1). This product was subsequently mineralized as confirmed by response time of chromatograms of LC-MS data. Intermediates, as identified in this study match with those predicted by Haque and Muneer, Sharma *et al.* [33–35]. Based on these identified intermediates, a pathway to complete mineralization is shown in Figure 9.

CONCLUSIONS

The photocatalytic oxidation of isoproturon has been studied using TiO_2 in slurry mode. The oxidation proceeds with first-order kinetics and parameters like photocatalyst concentration, pH, initial substrate concentration, UV intensity play important role affecting the photocatalytic reaction rate, thus deciding the optimized conditions. TiO_2 loading 0.5 g L^{-1}, pH 5.0, C_0 = 25 mg L^{-1} are the optimized conditions for obtaining the better degradation rates. The COD reduction (96%) and TOC reduction (90%) along with ammonium ion generation confirmed the mineralization of the herbicide, isoproturon through various intermediate compounds as evident through HPLC and LC-MS data. The observations, clearly demonstrates that outcome of the study can be suitably used for removal of Isoproturon from water/wastewaters using this technology as pre or post treatment.

ACKNOWLEDGMENTS

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LITERATURE CITED

1. Jumanah, F. (1994). Pesticide policies in developing countries: Do they encourage excessive use? World Bank Discussion Papers 238, The World Bank, Washington DC.
2. Farah, J. (1994). Pesticide policies in developing countries: Do they encourage excessive use? World Bank Discussion Papers 238, The World Bank, Washington DC, p. 42.
3. Dhaliwal, G.S. & Singh, B. (Eds). (1993). Pesticides: Their ecological impact in developing countries, New Delhi: Commonwealth Publishers.
4. Singh, H.K., Muneer, M., & Bahnemann, D. (2003). Photocatalysed degradation of a herbicide derivative, bromacil, in aqueous suspensions of titanium dioxide, Photochemistry and Photobiology Science, 2, 151–156.
5. Badawy, M.I., Montaser, Y.G., & Tarek, A. (2006). Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination, 194, 166–175.
6. Evgenidou, E., Bizani, E., Christophoridis, C., & Fytianos, K. (2007). Heterogeneous photocatalytic degradation of prometryn in aqueous solutions under UV-Vis irradiation, Chemosphere, 68, 1877–1882.
7. Lapertot, M., Ebrahimi, S., Dazio, S.. Rubinelli, A., & Pulgarin, C. (2007). Photo-Fenton and biological integrated process for degradation of a mixture of pesticides, Journal of Photochemistry and Photobiology A: Chemistry, 186, 34–40.
8. Segura, C., Zaror, C., Mansilla, H. D., & Mondaca, M.A. (2008). Imidacloprid oxidation by photo-Fenton, Journal of Hazardous Materials, 150, 679–687.
9. Andreozzi, R., Caprio, V., Insola, A., & Marotta, R. (1999). Advanced oxidation processes (AOP) for water purification and recovery, Catalysis Today, 53, 51–59.
10. Mohajerani, M., Mehrvar, M., & Ein-Mozaffari, F. (2009). An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment. International Journal of Engineering, 3, 120–127.
11. Kulshrestha G. & Muckerjee S.K. (1986). The photochemical decomposition of the herbicide isoproturon. Pesticide Science, 17, 289–494.
12. Perrin-Ganier C., Breuzin C., Portal J.M., & Schiavon M. (1996). Availability and persistence of isoproturon under field and laboratory conditions, Ecotoxicology and Environmental Safety, 35, 226–230.
13. Oller, I., Gernjak, W., Maldonado, M.I., Perez-Estrada, L.A., Sanchez-Perez, J.A., & Malato, S. (2006). Solar photocatalytic degradation of some hazardous water soluble pesticides at pilot-plant scale. Journal of Hazardous Materials, 138, 507–517.
14. Dionysiou, D. D., Khodadoust, A.P., Kern, A. M., Suidan, M.T., Baudin, I., & Laine, J.M. (2000). Continuous-mode photocatalytic degradation of chlorinated phenols and pesticides in water using bench-scale TiO2 rotating disk reactor, Applied Catalysis B: Environmental, 24, 139–155.
15. Lapertot, M., Pulgarín, C., Fernández-Ibáñez, P., Maldonado, M. I., Pérez-Estrada, L., Oller, I., Gernjak, W., & Malato, S. (2006). Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton, Water Research, 40, 1086–1094.
16. Haque, M. M. & Muneer, M. (2003). Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspensions of titanium dioxide, Journal of Environmental Management, 69, 169–176.
17. Sharma, M.V.P., Kumari, V.D., & Subrahmanyam, M. (2008). TiO2 supported over SBA-15: An efficient photocatalyst for the pesticide degradation using solar light. Chemosphere, 73, 1562–1569.
18. Parra, S., Malato, S., & Pulgarin, C. (2002). New Integrated photocatalytic-biological flow system using supported TiO2 and fixed bacteria for the mineralization of isoproturon, Applied Catalysis B: Environmental, 36, 131–144.
19. Burrows, H.D., Canle, L. M., Santaballa, J.A., & Steenken, S. (2002). Reaction pathways and mechanisms of photodegradation of pesticides, Journal of Photochemistry and Photobiology B: Biology, 7, 71–108.
20. Toor, A. P., Verma, A., Singh, V., Jotshi, C. K., & Bajpai, P. K. (2006). Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO2 in a shallow pond slurry reactor, Dyes and Pigment, 68, 53–60.
21. Ray, A.K. & Beenackers, A.C.M. (1998). Novel photocatalytic reactors for water treatment, AIChE Journal, 44, 477–483.
22. Harp, D.L. (2002). Total organic carbon (Direct method). U.S. Patent 6,368,870, April 09.
23. American Public Health Association (APHA). Standard Methods for the Examination of Water and Wastewater (19th Edition), APHA, Standard method no. (18th Edition), 4500-C, Washington, DC, 1992.
24. American Public Health Association (APHA). Standard Methods for the Examination of Water and Wastewater, (19th Edition), APHA, Standard method no. (18th Edition), 5220-C, Washington, DC, 1992.
25. Toor, A. P., Verma, A., Singh, V., Jotshi, C. K., & Bajpai, P. K. (2005). Photocatalytic degradation of 3,4 dichlorophenol using TiO2 in a shallow pond slurry reactor, Indian Journal of Chemical Technology, 12, 75–81.
26. Han, S.T., Li, J., Xi, H., Xu, D., Zuo, Y. & Zhang, J. (2009). Photocatalytic decomposition of acephate in irradiated TiO2 suspensions, Journal of Hazardous Materials, 163, 1165–1172.
27. Konstantinou, I.K. & Albanis, T.A. (2002). Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: Intermediates and degradation pathways, Applied Catalysis B: Environmental, 1310, 1–17.

28. Ollis, D.F., Pelizzetti, E., & Serpone, N. (1991). Destructure of water contaminants, Environmental Science & Technology, 25, 1523–1530.
29. Dubey, S. K., Kumar, A., Srivastava, P., & Anita, R. (2009). Solar photo-catalytic Treatment of Textile Wastewater for Biodegradability Enhancement I, Journal of Environmental Engineering, 152–164.
30. Toor, A. P., Verma, A., Singh, V., Jotshi, C. K., & Bajpai, P. K. (2007). Treatment of bleaching effluents from the pulp and paper industry by photocatalytic oxidation, Tappi Journal, 6, 9–13.
31. Reddy, P. A. K., Srinivas, B., Kala P., Kumari, V. D., & Subrahmanyam M. (2011). Preparation and characterization of Bi-doped TiO2 and its solar photocatalytic activity for the degradation of Isoproturon herbicide. Materials Research Bulletin, 46, 1766–1771.
32. Evgenidou, E., Fytianos, K., & Poulios, I. (2005). Photocatlytic oxidation of dimethoate in aqueous solutions, Journal of Photochemistry and Photobiology A: Chemistry, 175, 29–38.
33. Amorisco, A., Losito, I., Palmesano, F., & Zambonin, P.G. (2005). Photocatalytic degradation of the herbicide isoproturon: characterisation of by-products by liquid chromatography with electrospray ionisation tandem mass spectrometry, Rapid Communications in Mass Spectrometry, 19, 1507–1516.
34. Lopez-Munoz, M.J., Revilla, A., & Aquado J. Heterogeneous Photocatalytic Degradation of Isoproturon in Aqueous solution: Experimental design and intermediate products, Catalysis Today, in press. **http://dx.doi.org/10.1016/j.cattod.2012.11.0**.
35. Sharma, M.V. P., Kumari, V. D., & Subrahmanyam, M. (2008), Photocatalytic degradation of isoproturon herbicide over TiO2/Al-MCM-41 composite systems using solar light, Chemosphere, 72, 644–651.