

**Degradation Studies of Insecticide Imidacloprid Using
Fluidized Bed Photocatalytic Reactor**

**Submitted in partial fulfilment for the requirements of the
Degree of**

**MASTER OF TECHNOLOGY
IN
ENVIRONMENTAL SCIENCE AND TECHNOLOGY**

**Under the supervision of:
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Assistant Professor**



**Submitted by:
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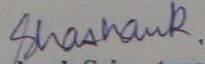
**SCHOOL OF ENERGY AND ENVIRONMENT
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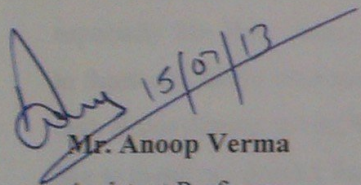
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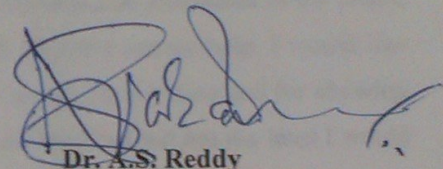
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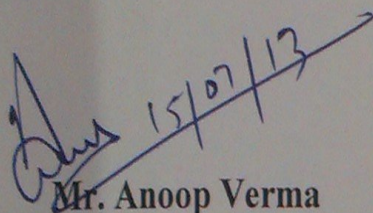

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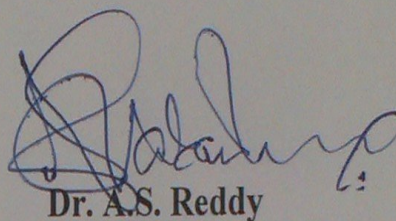
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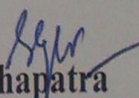
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ABSTRACT

Disposal and treatment of wastewater containing bio-recalcitrant such as insecticide imidacloprid is a matter of great concern. Various conventional and existing treatment technologies could only concentrate the pollutants by transferring them from one phase to the other. Moreover, the conventional treatments could also generate toxic secondary pollutants too, which further adds up the operational costs. Hence there is an urgent need to look for the advanced and emerging technologies which could completely mineralize the irrespective pollutants. Advanced Oxidation Process has emerged one such technology for treatment of such bio-recalcitrant compounds, which relies on the principle of production of high oxidation potential hydroxyl ions which ultimately converts the toxic compounds to non-toxic end products.

One such approach in AOP's include Fixed Bed Photocatalysis to treat pesticidal wastewater using suitable catalyst such as TiO₂ P-25 Degussa. Since the mode of catalyst usage and its recovery is a matter of concern from the economical point of view, hence the immobilization of catalyst onto suitable support material is the need of hour. Pebbles made out of cement and sand mixture proved to be mechanically robust, chemically inert and cheap immobilizing material which has the very high adsorptive capacity towards the catalyst with negligible catalyst attrition rate.

In the present study, 25 mg/L of pesticide imidacloprid solution was treated under optimized conditions and various parameters and degradation feasibilities were analyzed. Various diameters of immobilizing material were tried and the optimum results were found at 0.75 cm diameter along with catalyst loading of 3% (w/w), degradation was found out to be 81.1%. Effect of oxidant dose was also studied and the degradation occurred was as high as 88% under the optimum dosage of 4.8 ml/L.

CHAPTER-1

INTRODUCTION

Imidacloprid belongs to a new class of insecticides, called neonicotinoids. Since its launch in 1991, products containing imidacloprid have gained registrations in about 120 countries and are marketed for use in agriculture (for over 140 agricultural crops), on turf, pets and for household pests (**Elbert et al., 1991**). Imidacloprid acts as an agonist on the postsynaptic nicotinic acetylcholine receptors of motor neurones in insects. This causes an overstimulation of the nervous system, and ultimately kills the insect (**Kramer et al., 2001**).

1.1 Environmental impacts of Imidacloprid

Low vapour pressure and high water solubility of insecticidal wastewater suggests a potential to leach to ground water (**Bacey et al., 2000**). Its persistence in soil allows for continual availability for uptake by plant roots which allows it to rapidly move through plant tissues after applications, and can be present in detectable concentrations in tissues such as leaves, vascular fluids, and pollen. Many non-target beneficial arthropods such as honeybees, parasitic wasps, and predaceous ground beetles are sensitive to imidacloprid (**Anderson et al., 1997**).

These organisms may be adversely affected by sub-lethal doses of the insecticide, but the effects vary widely depending on application method and route of intake. There is a potential for stress-related sub-lethal effects on fish in water contaminated with imidacloprid (**CEI, 2003**). Since several imidacloprid metabolites have been shown to be equal or greater in toxicity than the parent compound, their presence in the environment is a great concern to deal with.

1.3 An Overview of Remediation Process

In order to achieve different levels of contaminant removal, individual waste-water treatment procedures are combined into a variety of systems which are classified as primary, secondary and tertiary treatments. However, conventional WWTPs or DWTPs are not designed for the treatment of wastewaters containing highly polar contaminants (**Xu et al., 2007**). Therefore, practical and economical solutions must be achieved in order to reduce the daily amounts of insecticide discharged into the environment. Depending on the pollutant concentration in the effluent and the cost of the process, a wide range of chemical and physical methodologies such as

chemical oxidation, biodegradation, adsorption, liquid extraction and membrane techniques etc. can be employed for the removal of organic compounds.

1.3.1 Conventional treatments

The biological processes, filtration and coagulation/flocculation/ sedimentation are the most used in conventional wastewater treatment plants.

In the biological systems, activated sludge technology is widely used, especially in industrial effluent treatments. The method consists of the organic compounds degradation in activated sludge tanks, with aerobic or anaerobic systems, by monitoring continuously temperature and the chemical oxygen demand (COD). In addition to it, biological processes took several days of operation (**Klaverioti et al., 2008**). The high toxicity of many contaminants prevents the application of this process in effluents with high pollutants concentration, since they are recalcitrant and toxic to the microorganisms (**Britto and Rangel, 2008**).

Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem (**Gaya and Abdullah, 2008**).

Currently available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but still remain and not being completely “eliminated” or “destroyed” (**Padmanabhan et al., 2006**).

Chlorination has been the most commonly and widely used disinfection process. The disinfection by-products generated from chlorination are mutagenic and carcinogenic to human health (**Yang and Cheng, 2007**).

As a result, implementation of advanced treatment technologies are required to achieve high-quality treated effluents (**Radjenovic et al., 2009**).

1.3.2. Modern Technologies

Among the emerging technologies, Advanced Oxidation Processes (AOPs) have already been used for treatment of waste-water containing recalcitrant such as pharmaceutical active compounds. . The rationales of these AOPs are based on the in-situ generation of highly reactive

transitory species for mineralization of refractory organic compounds, water pathogens and disinfection by-products (**Esplugas et al., 2002**). These technologies have some important advantages like (1) they are destructive, rendering almost always innocuous end products (2) they are mostly non-selective; thus, they can be used for a wide range of undesirable compounds (**Bahnemann, 1999; Chen et al., 1999**).

Heterogeneous photocatalysis on metal oxide semiconductor particles is an advanced oxidation technology (AOT), which has been shown to be an effective means of removing organic pollutants from water streams. However, the rate of the photocatalytic reaction is determined by the illuminated surface area of photocatalysts, light irradiance, reactants adsorption rate, and the properties of photocatalysts.

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. Moreover, it necessitates downstream separation and recycle of the catalyst and are inefficient and difficult to scale up. Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of removing the catalyst (**Noorjahan et al., 2002**).

Generally, the rate is not significantly great due to the low photo-efficiency. Thus commercialization of photocatalytic processes is still in its infancy. Reactor design can alleviate some of the problems and increase the efficiency of the photo-catalyzed process.

Researches have been carried out in various types of reactors such as fixed bed and fluidized bed. In fixed-bed type of operation, several formulations of catalyst are in use: powder particles and granules (**Vorontsov et al., 2000**). For fluidized-bed photocatalytic reactions, titania was deposited on various supports. It is believed that fluidized bed photocatalytic reactors are more advantageous than fixed -bed reactors because of good catalyst-light contact (**Yue et al., 1983**).

This study therefore focuses on the selection of the suitable supporting material for catalyst impregnation along with the selection of suitable model compound and looking for various other fabrication and operational aspects in fluidized bed react

CHAPTER-2

LITERATURE REVIEW

Numerous studies have already been done in fixed bed photocatalysis therefore an overview of it, in the form of literature review is must. After going through the literature review of fixed bed photocatalysis, fluidized bed photocatalysis would be reviewed.

Rao et al., (2003) impregnated the commercially available titania on soft pumice stone after fixing pellets on hard surface of cement or polycarbonate using thin film fixed bed reactor to degrade compounds like 3-nitrobenzenesulfonic acid (3-NBSA) and Acid Orange-7.

Granular activated carbon (GAC) fixed bed adsorption; the continuous photocatalysis systems and a combination of the two were studied by **Areerachakul et al., (2006)** to evaluate their capabilities in removing the herbicide of metsulfuron-methyl (MM) from waste water. Columns packed with GAC at different bed depths were operated at different filtration rates over a period of several weeks. Removal of MM via adsorption using GAC fixed beds of 5, 10 and 15 cm depths (operated at meter per hour) 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%.

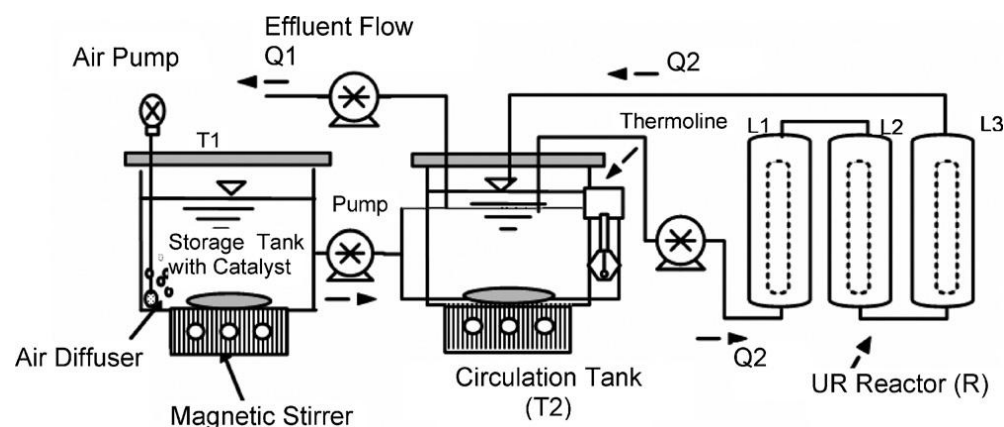


Fig-2.1 Schematic of the continuous flow photocatalytic reactor with the catalyst (T1, mixing tank with no light source; Q1, influent and withdrawal flow rate; Q2, re-circulation flow; T2, re-circulation tank; R, UV reactor unit; L1, L2, L3 are UV C lamps 8W each).

Table-2.1 Design Discussion of Continuous Flow Photocatalytic Reactor

TiO ₂ dosing rate	1.5 g L ⁻¹
Q2	100ml min ⁻¹
Capacity of reactor unit	70 ml each
Herbicide concentration	10 mg L ⁻¹

A photocatalytic reactor immobilized with titania on a glass plate was studied on a bench scale using solar irradiation by **Noguiera et al.,(1996)** takes into account the influence of parameters like slope of plate, light intensity, flow rate and geometry of the reactor to mineralize Dichloroacetic Acid.

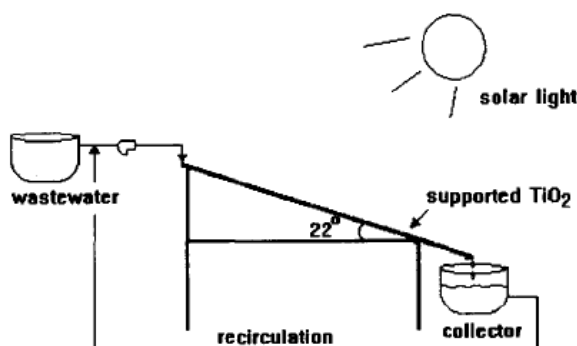


Fig-2.2 Schematic view of TiO₂-fixed-bed solar reactor.

Selva and Rajeshwari, (2003) reported the full decomposition of 500 ml, 200 mM reactive red 22 (RR 22) dye in 100 minutes in the presence of a thin film of ZnO photocatalyst using a thin film flat bed flow photoreactor under solar radiation.

Ghanem et al., (2009) investigated the performance of solar photocatalytic pilot plant using TiO₂-P-25 (Degussa) for removal of commercial azo dye and optimizing various parameters, influencing the performance of the operated thin-film fixed-bed reactor (TFFBR) and showed kinetic dependency on flow rate, catalyst loading, and initial dye concentration.



Fig-2.3 A Pilot Scale Thin Film Fixed Bed Reactor

Table-2.2 Design Discussion of Thin Film Fixed Bed Reactor

Dimensions of reactor	$(10 \times 2.5) \text{ m}^2$
Inclination angle	20°
Tank volume	1 m^3 each

Chan and Chan, (2002) constructed a photocatalytic cascade reactor consisting of nine stainless steel plates coated with titania to investigate the decomposition of benzoic acid in waste-water.



Fig-2.4 Cascade reactor

Table-2.3 Design Discussion of Cascade reactor

Supporting Material	Stainless Steel
Area of Reactor	17.5 x 28 cm ²
Flow Rate	2-5 l/min

Feitz et al., (2000) evaluate 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%.

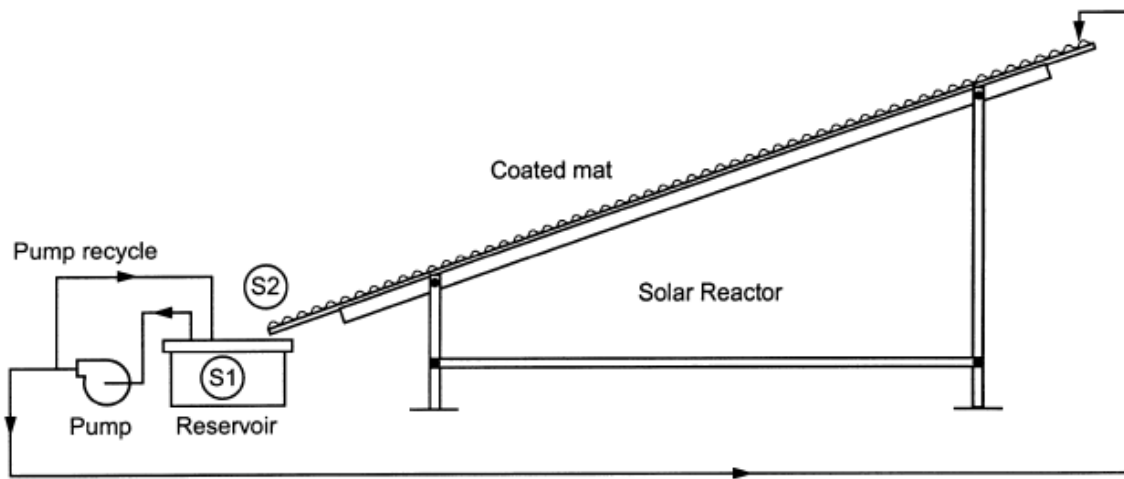


Fig-2.5 Coated Mesh Reactor

Table-2.4 Design Discussion of Coated mesh reactor

Supporting Material	Glass-fibre mesh
Area of Reactor	6.5x0.5 m ²
Flow Rate	5lt/min

Whereas packed bed reactor achieves 98% removal of phenol from a 2.3 mg/l of 100 l solution. The PBR processes a similar concentration of phenol approximately 7 times faster than does the CMR under similar light conditions. While the CMR does not require any additional air input, the air injection system forms an important component of the PBR treatment system providing mixing and ensuring sufficient oxygen is present.

Table-2.5 Design Discussion of Packed bed reactor

Supporting Material	Mirror-finish stainless steel
Area of Reactor	1x2 m ²
Flow Rate	3 lt/min

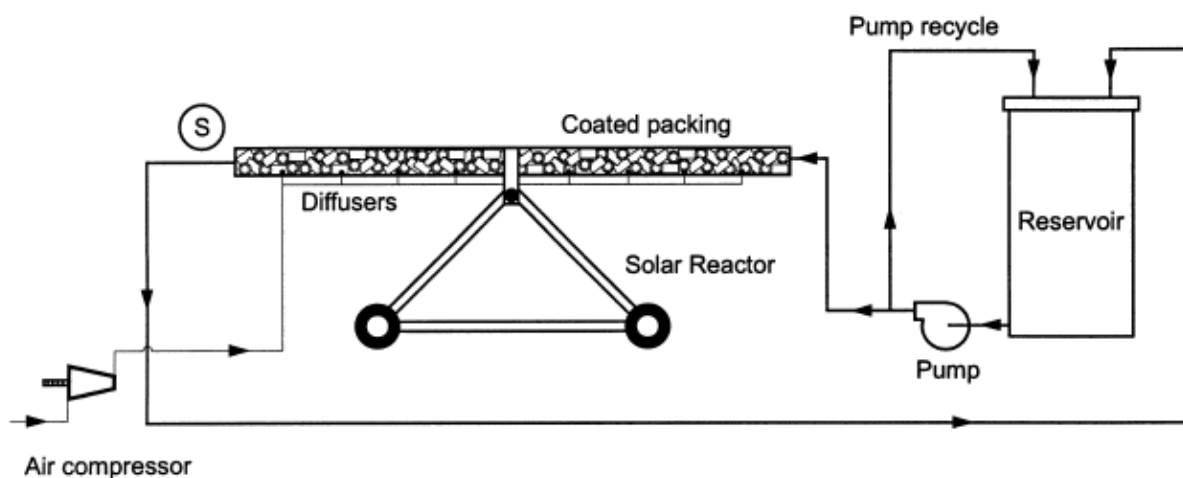


Fig-2.6 Packed Bed Reactor

Crittenden et al., (1997) the wastewater containing BTEX (benzene, toluene, ethyl benzene, o-xylene, m-xylene, p-xylene) partially with catalyst impregnated adsorption and partially with photocatalytic reactor.

Chiou and Shei, (2006) decomposed 5mg L⁻¹ di-n-butyl phthalate (DBP) upto 75% in 80 min. reaction time in a photoreactor containing glass beads coated with titania.

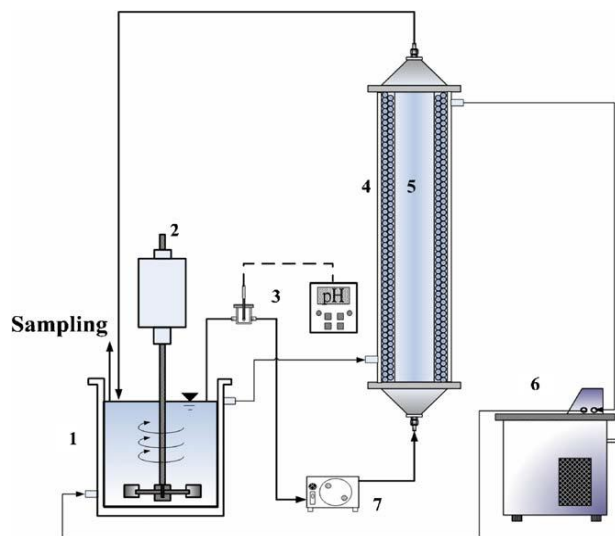


Fig -2.7 Sketch of the experimental apparatus. Components: (1) reaction vessel (2) stirrer, (3)pH meter, (4) photoreactor, (5) UV lamp, (6) thermostat, and (7)syringe pump

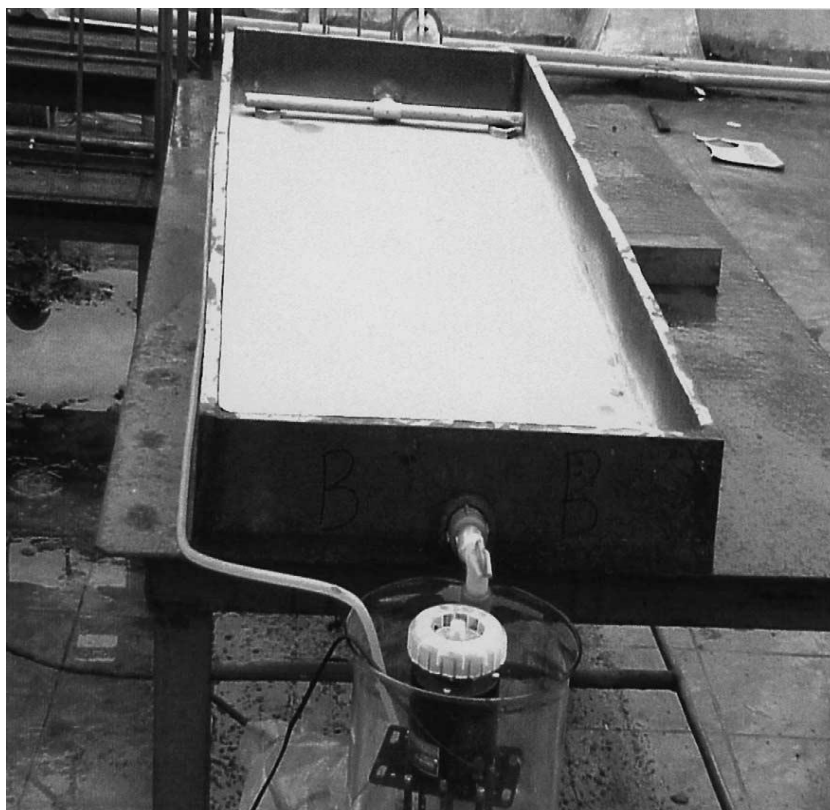
The inner diameter of the outer tube is 35mm and the outer diameter of the inner tube is 26 mm was deposited on the silicate glass beads ($d_p = 2$ mm). 0.5 g TiO_2 with 1mL water containing 0.1mL acetylacetone produces. Degussa P-25 TiO_2 a viscous paste, and then the paste was diluted by very slow addition of 1.7mL water. Finally 1 drop of Triton® X-100 was added to the paste and then the mixture is mixed with 15 g glass beads. After drying at 100°C for about 10 min, the TiO_2 with glass beads mixture was annealed in an oven at 450°C for 30 min. Subsequently, the $\text{TiO}_2/\text{glass}$ obtained was packed in the reactor and washed by 20 mL min^{-1} distilled water to remove the uncoated TiO_2 , which was collected and weighted. From the calculation, each gram $\text{TiO}_2/\text{glass}$ contains 0.02 g TiO_2 . The photoreactor was packed with 150 g $\text{TiO}_2/\text{glass}$, and the void volume of the photoreactor after packing is 55 ml. The total volume of the target DBP solution used in one experiment was 500 ml. The UV irradiation source was an 8W lamp encased in a quartz tube.

Malato et al., (2002) tested the granulated version of the well-known P-25 titanium dioxide over the powdered form to treat the wastewater containing dichloroacetic acid, phenol and

imidachlorpid in a pilot compound parabolic collector (CPC) plant and found that its not a good alternative due to the fact that it forms spontaneous sedimentation during the photocatalysis.

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 employs glass spheres dip coated with titania.

Noorjahan et al., (2002) studied the heterogeneous photocatalytic degradation of H-acid, a toxic and non-biodegradable dye intermediate, in TiO_2 suspensions and TiO_2 thin film fixed bed reactor.



**Fig-2.8 Photograph of TiO_2 TFFBR. Size: 144 cm \times 52 cm \times 10 cm;
solution flow rate: 750 ml min⁻¹; batch size: 5 l.**

Table 2.6 Design Discussion of TFFBR

Supporting Material	Cuddapah Stone
Size of Reactor	144x52x10 cm ³
Flow Rate	750 ml/min

Sarria and Kenfack, (2002) combined the solar-biological system at field pilot scale for the treatment of a model biorecalcitrant compound 5-amino-6-methyl-2-benzimidazolone (AMBI) and the mineralization observed was in the range of 80%-90%.

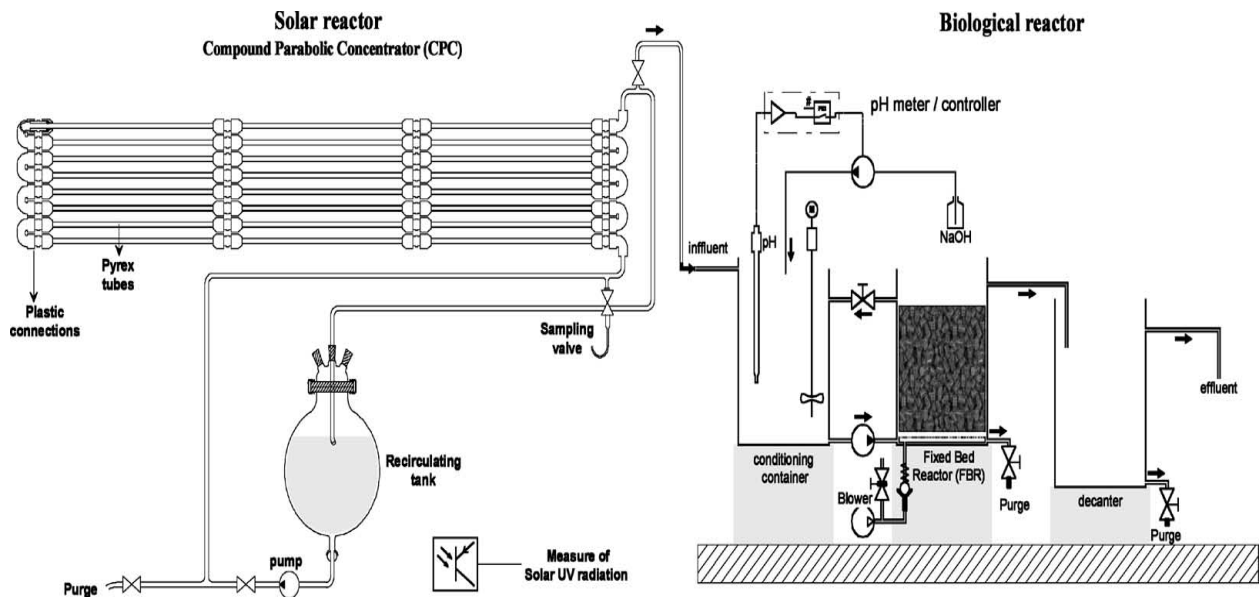


Fig-2.9 Schematic view of the coupled solar-biological flow reactor.

The coupled bioreactor consists of Compound Parabolic Solar Collector (CPC) and a bioreactor. CPC is a static collector with a reflective surface describing an in-volute around a cylindrical reactor tube. Due to the reflector design as shown almost all the UV radiation arriving at the CPC aperture area (not only direct, but also diffuse) can be collected and so be available for the process in the reactor. The UV light reflected by the CPC is distributed around the back of the tubular photoreactor and as a result, most of the reactor tube circumference is illuminated.

The CPC has three modules (collector surface 3.08m², photoreactor volume 24 l, and total reactor volume 60 l) whereas one module consists of eight tubes and mounted on a fixed platform 46° tilted (local latitude). The three modules are connected in series with water directly

flowing through them at 30 l min^{-1} , leading finally to a recirculation tank connected to a centrifugal pump.

The bioreactor consists of three modules: a 50-l conditioning container, a FBR, and a decanter. The conditioning container is equipped with a pH control unit. The photo-pretreated water is piped across the bottom layer to the FBR by means of a centrifugal pump. The FBR consist of a 43-l column containing plastic supports colonized by activated sludge. The effluent is circulated through the column which operates as an up-flow reactor. The top treated water over-flows to a 50-l decanter, where sludge is extracted.

Rao and Chaturvedi, (2012) investigated the decoloration and mineralization of textile wastewater using pebble coated with catalyst in the direct sunlight.

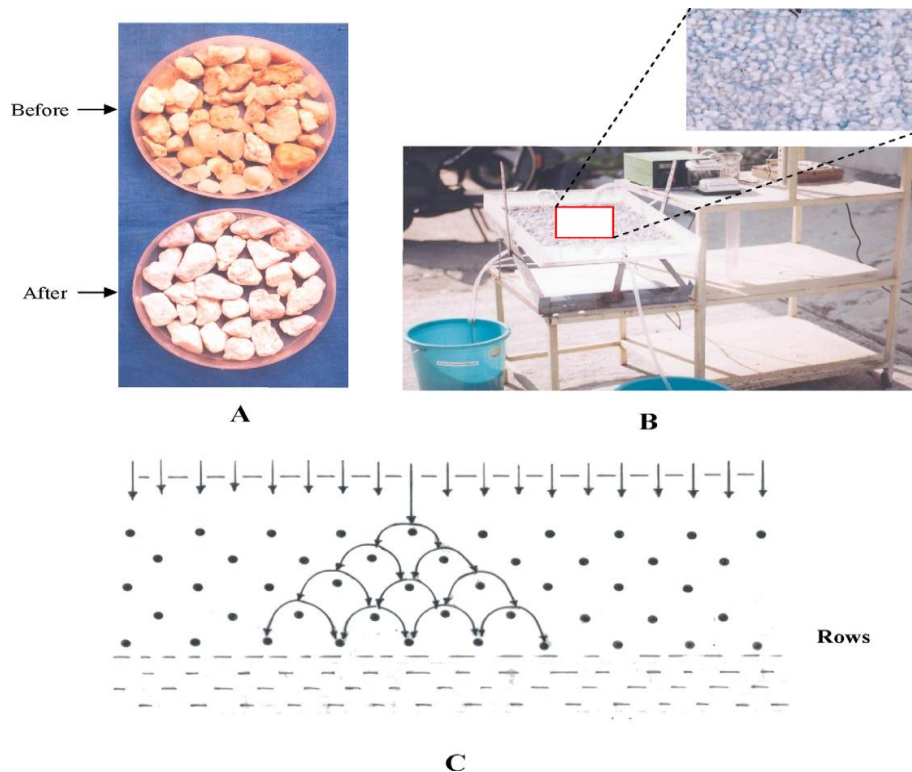


Fig-2.10Arrangement and distribution of pebbles.(A) Pebbles before and after TiO_2 coating, (B) solar photocatalytic pebble bed reactor and the close-up of pebbles, (C) arrangement of pebbles in a pebble-bed reactor and expected water distribution pattern (arrows indicate the direction of flow of water).

The trough (inner length, 52 cm; inner width, 45 cm; height, 0.8 cm) was fabricated using a transparent Perspex sheet. The pebbles position in an ordered configuration forming equilateral

triangles allows the optimal distribution of the liquid over the pebbles to avoid preferential channeling.

Remarks : In all the fixed bed reactors, either the suspension solution or the thin film is employed. In the suspension form, the slurry left at the completion of the reaction time needs to be further treated for the recovery of the catalyst and disposal of the used one. In case of thin film, the slurry problem do not arise but the catalyst keeps on withering away with each recycle from the film. Hence in both the cases, catalyst consumption rate is of great concern.

Vega et al.,(2011) reported the fluidized bed degradation of herbicide 2,4 dichlorophenoxyacetic acid (2,4-D) with template-free TiO₂ photocatalytic spheres in the presence of UV irradiation at 254 nm.

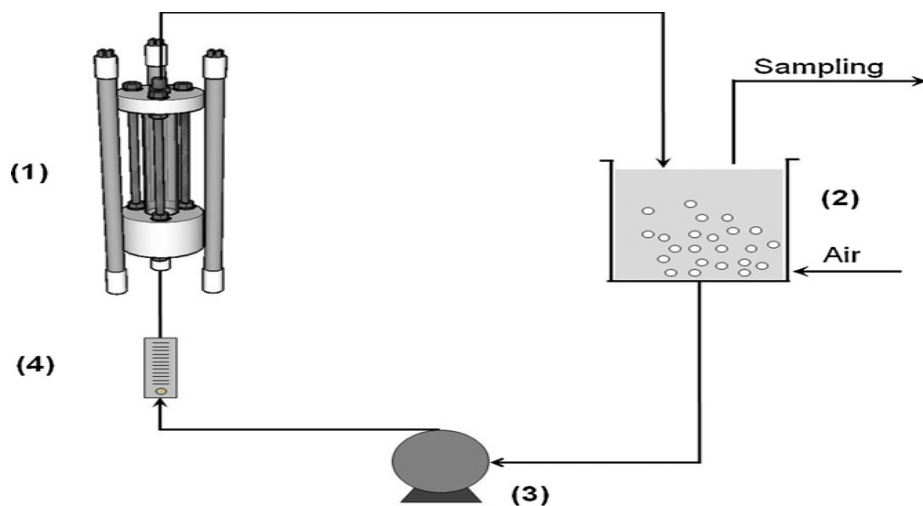


Fig-2.11 Experimental setup: (1) fluidized bed photocatalytic reactor (FBPR), (2) tank, (3) pump, (4) flowmeter and controller.

Farmarzpour and Vossoughi,(2008) studied the effects of initial concentration, catalyst mass/solution volume ratio, oxidant molar flow, residence time, and light intensity on process removal efficiency, and kinetics of the reactions for treating wastewater containing furfural in a floating bed photoreactor using low density and porous ‘perlite’ support and observed 95% concentration reduction in 2 hours.

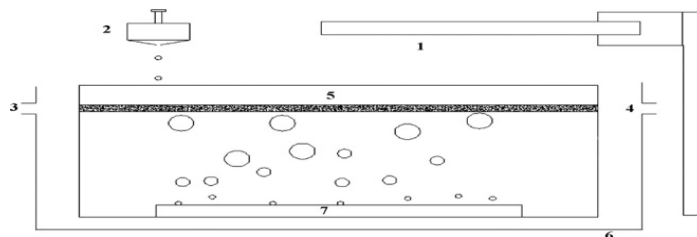


Fig-2.12 Scheme of the utilized floating-bed photoreactor. (1) Adjustable UV lamp; (2) chemical feed; (3) cooling water inlet; (4) cooling water outlet; (5) floating bed; (6) reactor jacket.

Table 2.7 Design Scheme of the utilized floating-bed photoreactor

Dimension	280mm×115mm×70mm
Solution Concentration	48-480 ppm
Volume taken	500 ml

Sanino and Vaiano, (2010) investigate the study which avoids the deactivation of sulphated MoOx/TiO₂ catalysts in the photocatalytic cyclohexane oxidative dehydrogenation by a fluidized bed photoreactor.

Imoberdorf et al., (2008) proposed a predictive model of the radiation distribution for fluidized bed photocatalytic reactors which considers the interaction between the photocatalytic TiO₂-coated spheres and the photons, taking into account the shadowing effect of the beads, the reflection on the surface of the spheres, and the absorption in the TiO₂ films.

King and Liang,(2008) deposited the atomic layer of controlled-thickness TiO₂ film on the particle substrates in a fluidized bed reactor. Films were deposited on 550 nm silicon dioxide spheres and 65 nm ZnO nanoparticles which were fluidized with the assistance of a magnetically-coupled stirring unit.

Continuous deduction of 1000 ppm toluene vapour in a multi-stage gas fluidised bed photoreactor using TiO₂ coated activated carbon (AC/TiO₂) particles as the fluidising media was studied by **Kuo et al., 2011**). The efficiency of the toluene removal from the gas stream by the

mass transfer-limited photocatalytic reaction was significantly improved using AC/TiO₂ particles as the fluidising media due to the enrichment of the local toluene concentration. The removal efficiency increases approximately by 3-4% at every stage.



Fig-2.13 Three stage fluidized bed system

Lim and Kim, (2003) determined the effects of trichloroethylene (TCE) gas flow rate, relative humidity, TiO₂ film thickness, and UV light intensity on the annulus fluidized bed photoreactor over the degradation of TCE.

Chongdian et al., (2012) studied the photocatalytic degradation of formaldehyde in a sound-magnetic assisted fluidized bed (SMFB) using Degussa P-25 catalyst and Fe₃O₄ particles as the fluidized media. The effects of magnetic induction, sound pressure level, and sound frequency on the degradation rate of formaldehyde were investigated and it was found that sound and magnetic assisted fluidized bed reactor (SMFB) enhances the degradation efficiency of formaldehyde effectively.

Lee et al., (2003) removed toxic microcystin-LR from water employing TiO₂-coated granular activated carbon in a fluidized bed photoreactor and shows how the adsorbed microcystin-LR migrated continuously onto the surface of TiO₂ particles which located mainly at the exterior surface in the vicinity of the entrances of the macropores of the activated carbon. The migrated microcystin-LR was finally degraded into nontoxic products and CO₂ very quickly.

Kabir et al., (2006) investigated the effects of hydrogen peroxide in a phenol treatment using a new composite photocatalyst that integrates titanium dioxide with an adsorbent zeolite supported

on glass beads implemented in a fluidized bed photoreactor and found out the advantageous use of the combination of photocatalysis with hydrogen peroxide over their individual use.

CHAPTER-3

OBJECTIVES

- Selection of suitable support for the catalyst with subsequent design of fixed bed reactor
- Degradation studies for the insecticide imidacloprid and process optimization including catalyst loading, oxidant dosage, dissolved oxygen, pebble diameter
- Recycling feasibility studies

CHAPTER-4

WORK ELEMENT & APPROACH

4.1 SELECTION OF SUPPORT MATERIAL

Since its been conferred from the literature reviews that slurry form of catalyst treatment is the an effective method but the separation of the catalyst from the slurry imposes the commercial implications, hence it is obvious to look for the material upon which the catalyst can be impregnated or the material in which the entrapment of the catalyst can be possible. The properties and characterization of the support material needed to be overviewed carefully. Parameters like inertness to the surrounding, being chemically and mechanically stable, and adsorptivity towards the catalyst, would be taken into account while selecting the cheap and eco-friendly supporting material for catalyst impregnation.

4.2 DESIGNING/ FABRICATING OF FLUIDIZED BED REACTOR

Since in a fixed bed photocatalysis the support material is fixed hence volume of wastewater flown per unit area of the material is less as compared to that in fluidized bed where the support material is in constant motion within the wastewater solution. Hence fluidized bed would be more efficient than the fixed bed.

Once the catalyst supporting material has been selected, it has to be decided whether the catalyst should be immobilized or entrapped into the material.

Therefore, various designing aspects such as the dimensions, capacity of the reactor, ways to increase the contact time etc needs to be designed.

4.3 PROCESS OPTIMIZATION

Once the support material and the pathway to degrade the recalcitrant is decided, a wholesome study would be required to done to measure the effects of various parameters like concentration

of catalyst, H_2O_2 , effect of UV intensity on degradation rate of these compounds and their kinetic studies to foresee the more economic viable method for maximum degradation rate.

5.4 RECYCLING QUOTIENT

The main strength of any waste-water treatment process lies in efficiency to which it can mineralize the wastewater and the recycling quotient of the component catalyst.

In this context, efforts shall be made to recycle or re-use the immobilized beads for the optimum 8-10 times without the loss of any catalytic activity.

CHAPTER-5

MATERIALS AND METHODS

5.1 Insecticide Imidacloprid

The solution of 25 ppm of Imida solution was prepared and the wavelength scan of the compound was taken with the help of UV-VIS spectrophotometer and highest absorbance was observed at 269 nm.

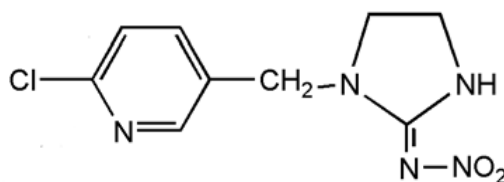


Figure 5.1: Structure of Imidacloprid

5.2 Reagents and Chemical Used

For carrying out experiment, photocatalyst was chosen as P-25 TiO₂ which is essentially a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, procured from Degussa Company, Mumbai).

Hydrogen Peroxide from Ranbaxy Laboratories was used as an oxidant.

Double Distilled water was used to prepare the catalyst slurry.

HCl and NaOH of N/50 strength were used for adjustment of pH of stock solution.

5.3 Instruments Used

5.3.1 pH meter

pH meter (CP 901) from Century Instrument Company was used measure the pH of the solution.

The pH of the solution was adjusted by adding HCl/NaOH drop-wise. Instrument was calibrated time to time with freshly prepared buffer solution (of pH = 4 and pH =9).

5.3.2 Spectrophotometer

Wavelength scan of the pesticide solution and its absorbance after definite time interval was taken with UV-VIS Spectrophotometer (Hitachi V- 500 UV/VIS (Japan) double beam spectrophotometer.

5.3.3 Branson Bath Sonicator

The catalyst TiO_2 form clusters of tiny lumps when its slurry solution is prepared for the coating purpose. Hence the slurry solution is kept in sonicator for 30 minutes so that these tiny lumps too dissolve to give the homogenous solution.

5.3.4 Muffle Furnace

Temperature controlled muffle furnace was used to immobilize the catalyst onto the support. The supporting material is calcined at 350°C for 1 hour.

5.3.5 Water Pump

A water pump of maximum capacity of 746 W along with the flow rate control nozzle was used to fluidize the supporting material through the reactor and to re-circulate the wastewater from the bucket reservoir to the reactor.

5.3.6 Radiometer

UV Intensity was measured with Eppley (model no. 33013) radiometer.

5.3.7 Vernier Caliper

The diameter of the immobilizing material was measured with vernier caliper which has the least count of 0.1.

5.4 Reactor Designing

The reactor is initially designed with the concentric cylindrical type of structure, the inner diameter carries the UV bulb/UV tube while the outer diameter carries the waste-water to be treated. The outer diameter contains the cement pebbles coated with the catalyst Titanium Di-

Oxide which gets fluidized all over the reactor length with the pressure of motor pump. The length of the reactor is kept out to be 40 cm. The outer diameter (carrying wastewater along with cement pebbles) is made to fabricate for 3 different sizes viz. 4.5 cm, as shown in fig 5.4.2 (reactor-2) 6 cm and 12 cm while the inner diameter (which is meant for UV source) is kept constant with 40 mm. Depending upon the different sizes of diameters, the capacity volume of waste-water to be treated also varies. The design with 6 cm outer diameter carries the capacity of 2.5 ltrs and gives out the best degradation result amongst of all the other 3 designs.



Fig- 5.4.1 Reactor-1

Outer Diameter =6 cm

Capacity = 2.5 ltrs

Height = 40 cm



Fig-5.4.2 Reactor-2

Outer Diameter = 4.5 cm

Capacity = 350 ml

Height = 20 cm

As shown in Fig- 5.4.1, the pilot scale fluidized bed reactor (reactor -1) is supported by holding stand. The solution of pesticide named Imida-chloropid is prepared upto 2.5 ltrs. in an aluminium bucket.

Pipe fittings were made appropriately, the inlet pipe being connected to the motor pump and the outlets were connected back to the bucket of imida solution. UV bulb of 250 watt was chosen as a source of UV and was inserted into the inner diameter.

Since, UV bulb is of high power, it generates a lot of heat energy, which ultimately gets transmit into the wastewater solution. To get rid of heating problem, double jacketed bucket system was introduced. The space b/w the two concentric buckets was ran through with the cold water, which cools down the excessive heat of the imida solution.



Fig.5.4.3 - Double Jacket : Front View



Fig.5.4.4 - Double Jacket : Top View

5.5 Experimental Operation

The pesticidal waste-water solution was made to circulate through the reactor with the help of the water pump. The high pressure of the pump causes the coated cement pebbles to get fluidized throughout the reactor volume. A set of air spargers, too, was provided to the waste-water solution for continuous air supply. In the presence of UV source, along with air source and immobilized catalyst onto the pebbles, degradation of waste-water starts occurring.



Fig-5.5.1 Titania Coated Cement Pebbles in a Fluidized Stage

5.5 Immobilizing Material

5.5.1 Preparation of immobilizing material

The paste of cement and sand and catalyst was prepared in a fixed ratio, and out of it small pebbles were made out. These pebbles were left for overnight in tap-water for curing.

On the other hand, a slurry of 2% (w/v) titanium dioxide was prepared in distilled water and all the pebbles were left in a slurry solution overnight for catalyst coating.

However, when the coated pebbles were employed in the experimental set up, it was seen that the catalyst is constantly washed away under the pressure of water pump. To overcome this problem of catalyst attrition, the paste of cement, sand and catalyst itself was tried in specific

ratios and pebbles, thus made, were left for overnight curing and it was found that the attrition rate has become as low as 0.2%

5.5.2 Size selection of the immobilizing material

Efforts were made to make the immobilizing material of nearly spherical size of different diameters. The diameter of each immobilizing material was taken 3 times with vernier caliper and the mean was taken to determine the diameter of the individual material. In this way diameter of all the materials were calculated out. Finally, the grand average was taken. Following this procedure, the diameter of 0.3 cm, 0.5 cm and 0.75 cm was made out. The diameter of greater than 0.9 cm was too heavy to get fluidized. The material with diameter 0.3 cm was too fragile whereas due to loose compaction the material with 0.3 cm diameter, catalyst attrition occurs. Material with 0.75 cm diameter holds the tight compaction and thus, was, chosen as the immobilizing material.

CHAPTER-6

RESULTS AND DISCUSSION

6.1 Standard Curve for Imidacloprid

Fig-7.1 shows the standard curve for Imidacloprid which is prepared by plotting the absorbance of Imida solution of varying concentration ranging from 5 ppm to 25 ppm at 269 nm. From this graph the unknown concentration for Imida solution can be determined.

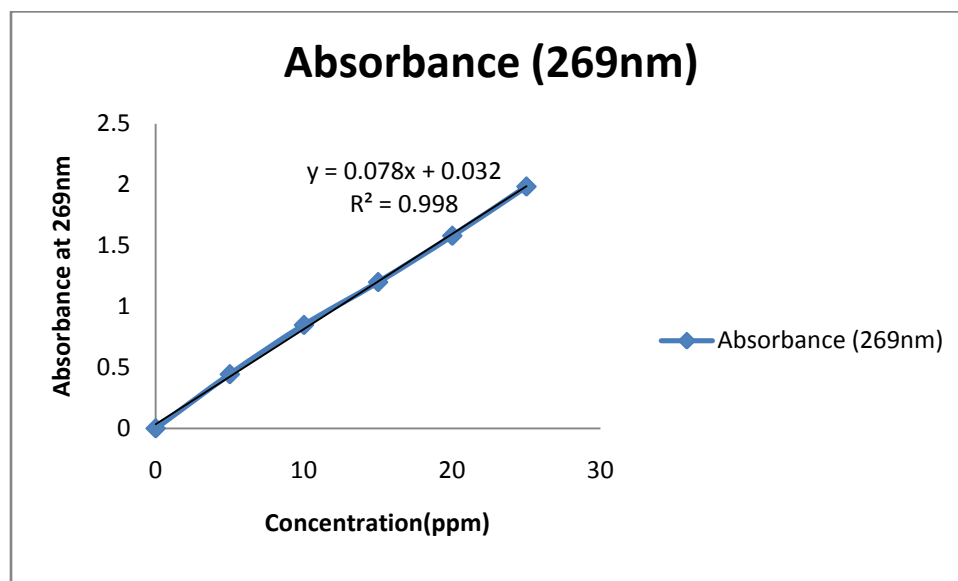


Fig-6.1: Standard Curve for Imidacloprid

6.2 Preliminary Studies:

Negligible degradation was found when an aqueous solution of Imidacloprid was treated in dark (catalyst only) and also in the absence of catalyst (light only) with the respective degradation of only 3% and 5% only. This simply implies that the light energy as well as the catalyst is required for the reaction to began. The use of oxidants such as H_2O_2 , too, results degradation of as low as 7%. The combination of UV- light and H_2O_2 only results in 10% degradation. Hence, it simply implies that the reaction required necessarily for degradation to take place required the simultaneous presence of TiO_2 , UV and oxidant.

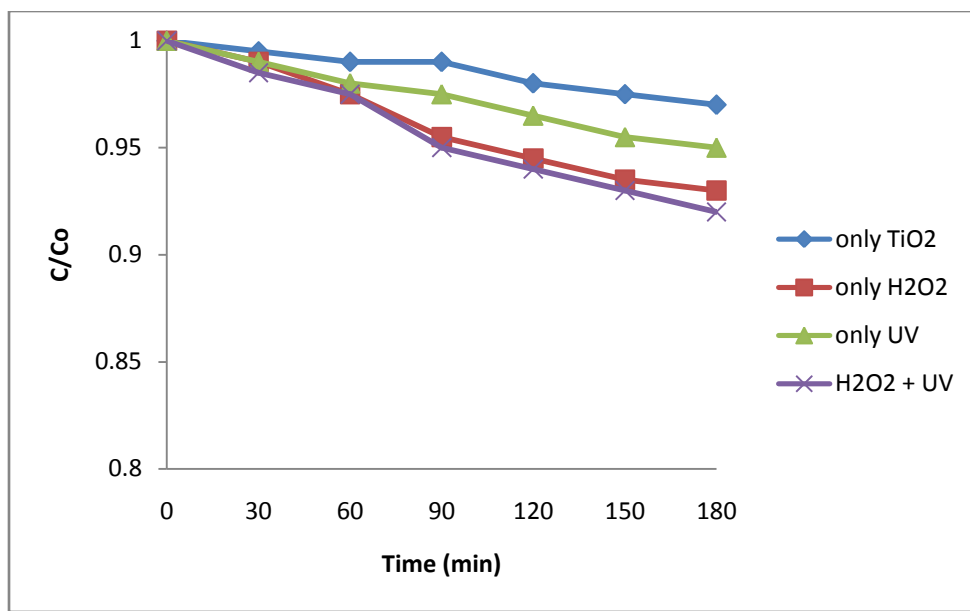


Fig 6.2 Preliminary Studies of Imidaclorpid

6.3 Photocatalytic treatment

The preliminary studies suggests the need of effective treatment for the complete mineralization of the compound. Therefore, advanced oxidation process is suggested for the treatment purpose of imidaclorpid solution before it gets discharged into the water bodies. Once Imida solution is subjected to photo-catalytic treatment, parameters like catalyst dose, pebble diameter, oxidant dose, effect of UV light, and effect of oxygen source are varied to obtain the optimized results.

6.4 Effect of Catalyst Loading

As discussed in the preparation of immobilizing material (5.5.1), the catalyst titania itself was mixed up with the sand + cement paste in varying amount in grams. Hence, according to the ratio of mixture, various amount of catalyst were made to mix, ranging from 1% to 5% (w/w). The degradation efficiency was found to be increased significantly upto catalyst loading of 3% (Fig.6.4). This is due to the fact that larger the no. of catalyst particles, larger will be the absorption of photons (**Balcioglu A.I. and Cecen F. T., 1999**). Further increase of catalyst amount results in further increase in degradation but the rate constant do not increased significantly. This can be explained by the fact that the no. of active site of the particles did not increase significantly with further increase in catalyst particles (**Toor A.P. et al., 2007**). Also the increased catalyst particles tends to hinder the UV light scattering, therefore the degradation efficiency

tends to become constant at certain amount of catalyst loading and began to decrease after certain amount of loading. Hence, the optimum titania loading was found to be 3% (w/w) with cement + sand paste.

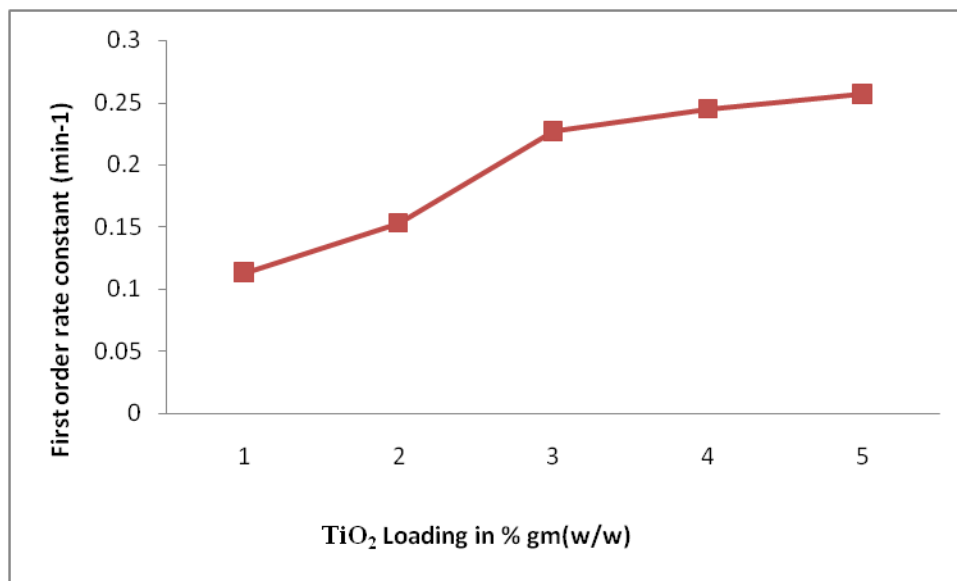


Fig 6.4: Optimization of Catalyst: 3% (w/w)

6.5 Effect of Pebble Size

The pebbles were made for 3 different sizes of approximate diameter 0.3 cm, 0.5 cm 0.75 cm. The pebble size with 0.3 cm diameter was too fragile to withstand the flow rate of wastewater and lacks robustness to last long. Hence, there occurs the high attrition rate of catalyst which ultimately leads to degradation as low as 10 % (Fig 7.4).Pebble size with diameter 0.5 cm withstand the flow rate of wastewater. However, catalyst attrition, too, occurs in it due to loose compaction of the pebbles. Pebble size with diameter 0.75 cm diameter was found to have a rigid compact, which results in very low attrition rate and robust enough to withstand with the fluidization flowrate.

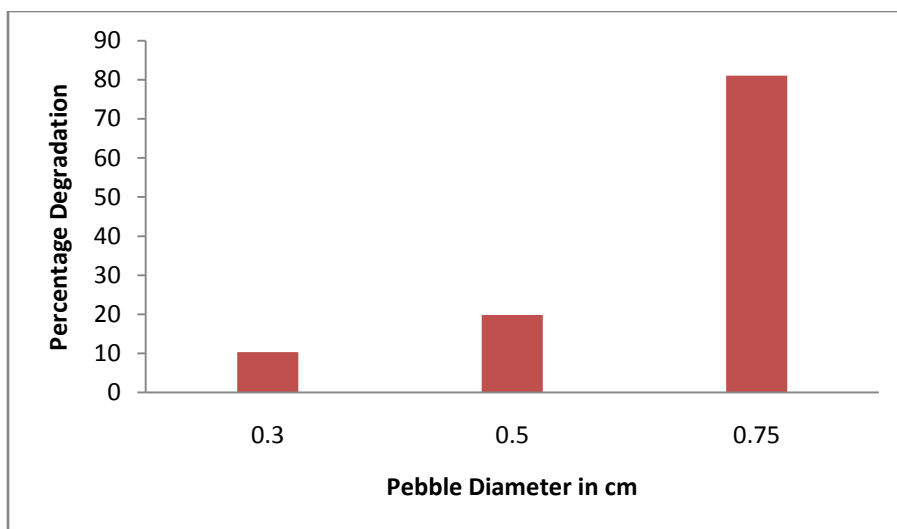
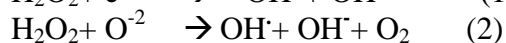


Fig 6.5 : Optimization of pebble size : 0.75 cm diameter at 3% (w/w) catalyst loading

6.6 Effect of oxidant addition

The addition of powerful oxidizing species such as H_2O_2 or $K_2S_2O_8$ to the titania suspension leads to the increase in the rate of photo-oxidation (Graetzel et al., 1990). H_2O_2 accepts a photo-generated electron from the conduction band and promotes charge separation (eq.1). It also forms OH^\cdot radicals (eq.2) (Pelizzetti et al., 1991).



Due to the high volume of the wastewater with net volume as high as 2.5 litres, the H_2O_2 concentration was varied from 1.6 ml/L to 8 ml/L at a fixed catalyst loading of 3% (w/w). The degradation of the wastewater was found to be as high as 88% under the oxidant dosage of 4.8ml/L (Fig 7.5). With the further increase in oxidant dose, the rate of degradation starts decreasing (Davis and Huang, 1990). This is due to the fact that at higher concentrations the production of hydroxyl radical occurs by photo-dissociation of H_2O_2 which ultimately consumes up the OH^\cdot required for the photo-catalytic reaction (Toor A.P. et al., 2005). This phenomenon is known as scavenging.

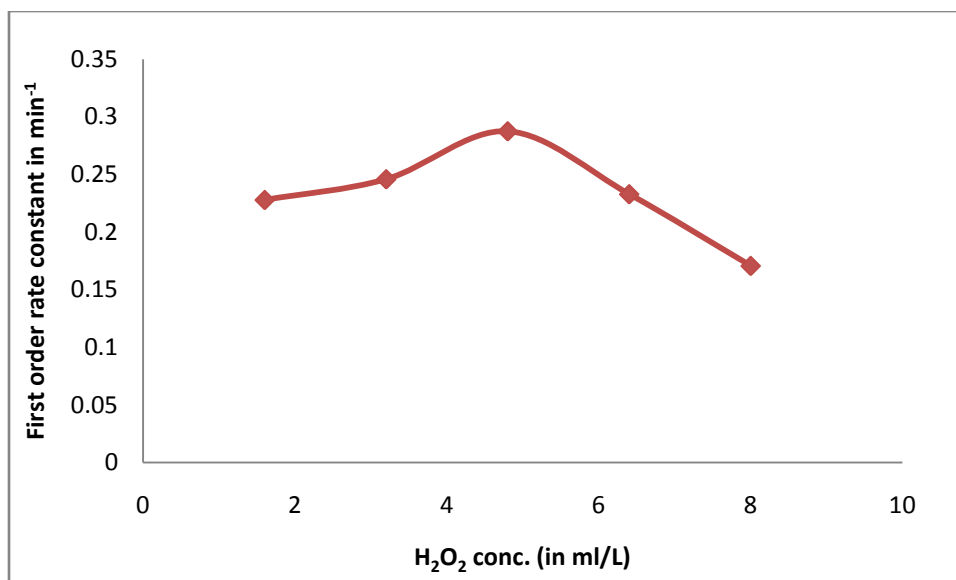


Fig-6.6: Optimization of Oxidant Dosage: 4.8 ml/L at 3% w/w catalyst loading with pebble diameter =0.75 cm

6.7 Effect of UV Intensity

The effect of UV intensity too was studied by varying the position of the UV rod from the base of the reactor. Three positions were chosen as 2 cm, 4 cm, 6 cm and 8 cm from the bottom of the reactor. Accordingly, the fluence rate is maximum at the bottom and minimum at the upper positions. With the help of the radiometer the intensities at these 3 positions were found to be 24 W/m², 18 W/m², 15 W/m², and 10 W/m². The degradation rate constants found to be maximum at 24 W/m² (Fig 7.6).

At higher intensities of light irradiation, the enhancement was considerably higher due to the predominant electron-hole formation. However at lower light intensity, electron-hole separation competes with recombination, which in turn decreases the formation of free radicals, thus causing lower degradations (**Bahnemann, 1999**).

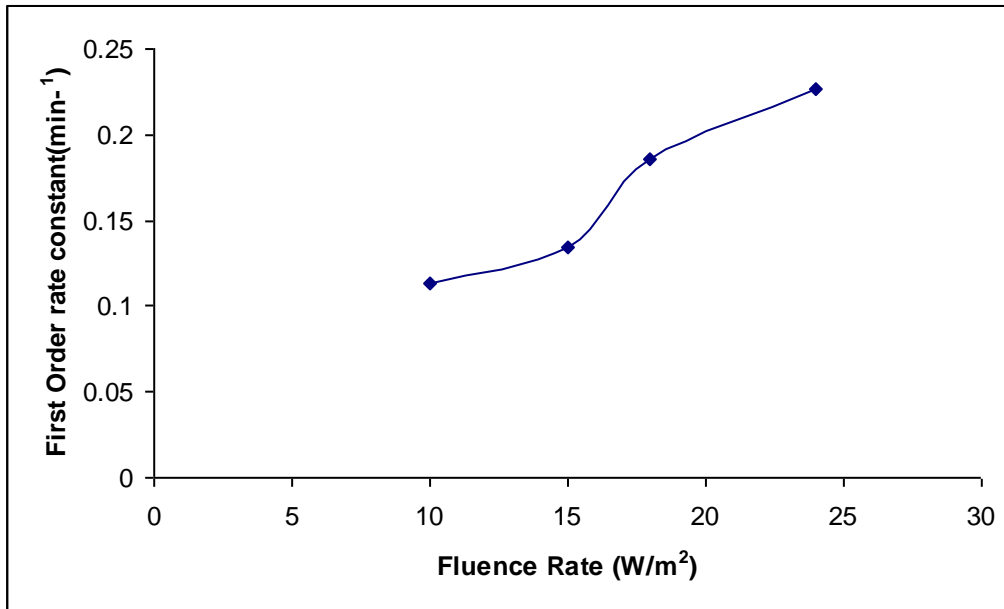
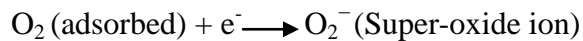


Fig 6.7: Optimization of fluence rate : 24 W/m² at catalyst loading =3%(w/w), pebble diameter=0.75 cm and oxidant dose = 4.8 ml/L

6.8 Effect of dissolved oxygen

Dissolved oxygen (DO) plays an important role in titania photocatalysis reaction to assure sufficient electron scavengers present to trap the excited conduction-band electron from recombination (Chong et al., 2009).



The superoxide ion coupled with H₂O₂ is found to have redox potential of equal to or greater than +0.36 V which is high enough to degrade a large variety of pesticides including imidacloprid (Rao and Hayon, 1973). In the present study, oxygen was supplied by the oxygen spargers and experiments were carried out, with and without oxygen source to observe its effect on the degradation of Imida wastewater solution.

It was observed that under optimized condition of 3% (w/w) of catalyst loading the degradation was found to be as high as 81.1% with oxygen source provided. However, without providing any oxygen source, the degradation reduces to 70% (Fig 6.8).

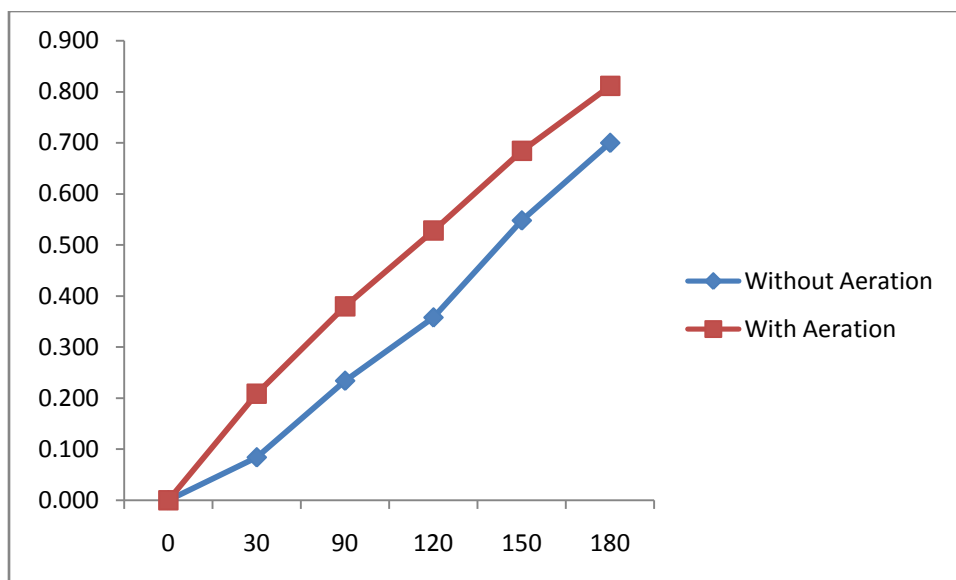


Fig 6.8: Comparison of degradation with and without aeration (x-axis: Degradation time in minutes; y-axis: Degradation per 100)

6.9 Comparison between slurry form, fixed bed and fluidized bed photocatalysis

During the lab scale preliminary studies, 200 ml solution of pesticidal wastewater was treated under slurry form, fixed bed form and fluidized bed form with (3% w/v) catalyst loading. Owing to the maximum no. of active particle sites available to photon interaction (**Toor A.P. et al., 2007**) the degradation was found to be maximum as high as 93% within 3 hours (Fig 7.8).

In the fixed bed photocatalysis, the catalyst got immobilized onto the support, hence the no. of active sites available for the reaction gets reduced. Hence, it will take more time to achieve the degradation rate as high as that in slurry form. Moreover, the mass transfer limitations also limits the overall efficiency to just 70% after 180 minutes (**Ballari et al., 2009**).

However, there is no mass transfer limitation in fluidized bed photocatalysis and the larger area of catalyst/volume of wastewater ratio make it more efficient than the fixed bed photocatalytic treatment (**Pozzo R.L., et al., 2000**).

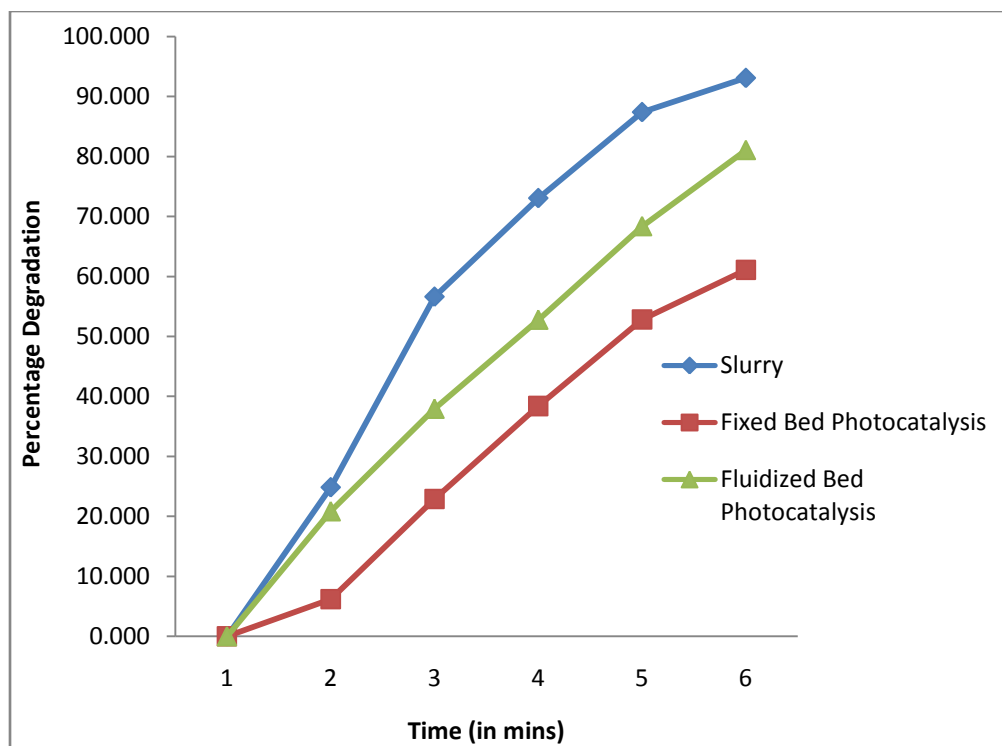


Fig 6.9 : Comparison between slurry treatment, fixed bed photocatalysis and fluidized bed photocatalysis

6.10 Recycling Feasibilities

Since the catalyst mixing with immobilizing material at the initial stage proved to be mechanically robust, chemically inert and the stable fixation of catalyst onto the support, hence it is expected that the catalyst laden pebbles can be used for time and again to treat the wastewater for multiple number of times. However with each cycle of operation, the attrition of catalyst particles lead to somewhat decreased efficiency of degradation. After 10th recycles the efficiency found was as good as 61% and the calculated attrition rate was found to be as low as 2%.

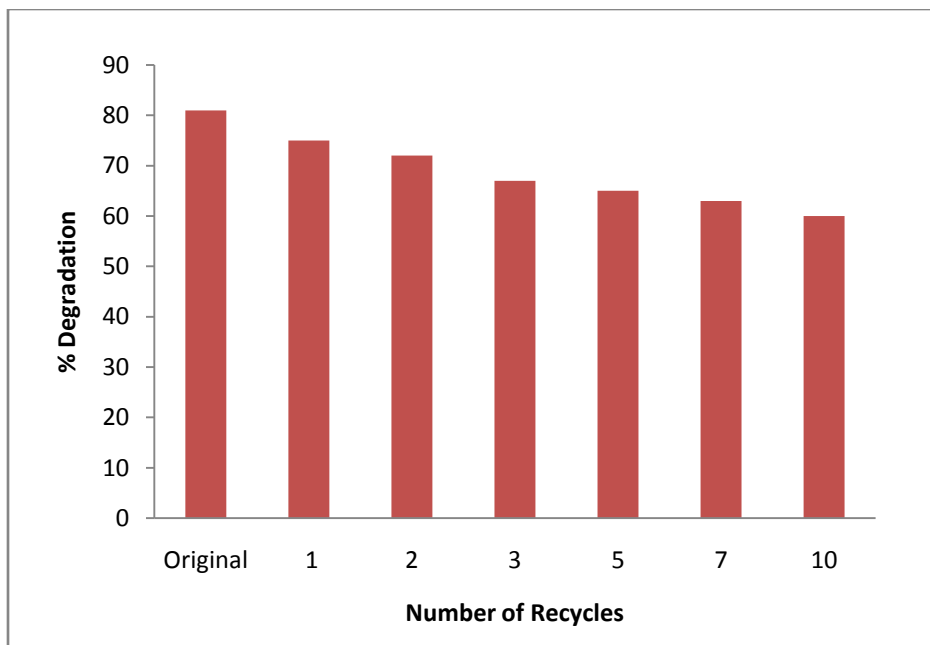


Fig 6.10: Comparison between the recycling efficiency at 3% (w/w) catalyst loading

CHAPTER-7

CONCLUSION

Under the optimized conditions the fluidized bed photocatalysis proved to be an efficient way to treat the imidacloprid wastewater. Since there is no mass transfer limitation in the fluidized bed photocatalysis, hence time taken by fluidized bed treatment is more efficient than the fixed bed photocatalysis.

The catalyst laden cement beads were mechanically robust and holds the catalyst for a longer time period. Hence, these beads can be used for recycling purposes. Therefore, it is an economical way to treat pharmaceutical wastewater, with the high reusability quotient of the catalyst.

All experimentations were carried out under UV tube. However, the tropical countries can harness the availability of solar irradiation to carry out fluidized bed photocatalysis.

CHAPTER-8

References

Anderson, J.P.E. (1995). Mineralization of [imidazolidin-4,5-¹⁴C] NTN 33893 to ¹⁴CO₂ in sterile and microbiologically active samples of 2 agricultural soils. Report No. 107300.

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

Bacey, J. (2000). Environmental fate of imidacloprid. *Environmental Monitoring and Pest Management Branch. Department of Pesticide Regulation*, 415-419.

Bahnemann, D. (1999). Photocatalytic detoxifications of polluted waters. In :*The Handbook of Environmental Chemistry. Vol.2, PartL : Environmental Photochemistry. Berlin: Springer-Verlag.*

Balcioglu, A.I., Cecen, F. T. (1999). Treatability of Kraft pulp bleaching wastewater by biochemical and photocatalytic oxidation. *Water Science Technology*.40 (1), 281–288.

Ballari, M.D.M., Alfano, O.M., Cassano, A.E. (2010). Mass transfer limitations in slurry photocatalytic reactors. *Elsevier*, 229-235

Baskaran, S., Kookana, R.S., Naidu, R. (1997). Determination of the insecticide imidacloprid in water and soil using high-performance liquid chromatography. *Journal of Chromatography A* 787(1-2), 271-275.

Britto J.M., Rangel, M.C. (2008). Processes advanced oxidation of phenolic compounds in industrial effluents. *New Chemistry, São Paulo. vol.31*,114-122

CEI (Cantox Environmental Inc.). 2003. Review on pesticide use research and monitoring activities in the maritime region (Nova Scotia, New Brunswick and Prince Edward Island). *Marine Environmental Sciences Division, Department of Fisheries and Oceans.*

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

Chiou, C.S., Shie, J.L., Chang, C.Y., Liu C.C, Chang, C.T. (2006). Degradation of di-n-butyl phthalate using photoreactor packed with TiO₂ immobilized on glass beads. *Journal of Hazardous Materials B137* , 1123–1129.

Chong, M.N., Lei, S., Jin, B., Saint, C., Chow, C.W.K. (2009). Optimization of an annular photoreactor process for degradation of Congo red using a newly synthesized titania impregnated kaolinite nano-photocatalyst. *Separation Purification Technology*, 67, 355-363.

Crittenden, J.C, Suri, R.P.S., Perram, D.L, Hand, D.W. (1997). Decontamination of wastewater using adsorption and photocatalysis. *Water Research* Vol. 31, No. 3 , 411-418.

David, A.P., Huang, C.P.,(1990), *Water Science Technology*,21:455

Esplugas, S., Contreras, J. G. S., Pascual, E., Rodriguez, M. (2002). Comparison of different advanced oxidation processes for phenol degradation. *Water Research* 36 , 1034-1042.

Faramarzpour, M., Vossoughi, M., Borghei, M. (2009). Photocatalytic degradation of furfural by titania nanoparticles in a floating-bed photoreactor. *Chemical Engineering Journal* 146 , 79–85.

Feitz, A.J., Boyden, B.H., Waite, T.D. (2000). Evaluation of two solar pilot scale fixed -bed photocatalytic reactors. *Water Research*, Vol. 34, No. 16 , 3927-3932.

Graetzel, G., Jirousek, J and Graetzel, M.(1990). Decomposition of organophosphorous compounds on photoactivated TiO₂ surfaces. *J. Molecular Catalysis* 60, 375-387.

Ibrahim, G.U., and Abdullah, A.H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J. Photochemistry Photobiology C: Photochemistry Rev.* 9 , 1-12.

Imoberdorf, G.E., Taghipour, F., Keshmiri, M., Mohseni, M. (2008). Predictive radiation field modeling for fluidized bed photocatalytic reactors. *Chemical Engineering Science* 63 , 4228-4238.

Jones, O.A.H., Voulvoulis, N., Lester, J.N. (2002). Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. *Water Research*, 36 , 5013-5022.

Kabir, M.F., Vaisman, E., Langford, C.H., Kantzas, A.(2006). Effects of hydrogen peroxide in a fluidized bed photocatalytic reactor for wastewater purification. *Chemical Engineering Journal* 118 , 207–212.

King, D.M., Liang, X., Zhou, Y., Carney, C.S., Hakim, L.F., Li, P., Weimer, A.W. (2008). Atomic layer deposition of TiO₂ films on particles in a fluidized bed reactor. *Powder Technology* 183 , 356–363.

Kramer, F., Mencke, N. (2001). *Flea Biology and Control: The Biology of the Cat Flea, Control and Prevention with Imidacloprid in Small Animals*, 217-218.

Kuo, H.P., Wu, C.T., Hsu, R.C. (2011). Continuous toluene vapour photocatalytic deduction in a multi-stage fluidised bed. *Powder Technology* 210 , 225–229.

Lee, D.K., Kim, S.C., Cho, I.C., Kim, S.J., Kim, S.J. (2004). Photocatalytic oxidation of microcystin-LR in a fluidized bed reactor having TiO₂-coated activated carbon. *Separation and Purification Technology* 34 , 59–66.

Lim, T.H., Kim, S.D. (2004). Trichloroethylene degradation by photocatalysis in annular flow and annulus fluidized bed photoreactors. *Chemosphere* 54 , 305–312.

Malato, S., Blanco, J., Campos, A., Cáceres, J., Guillard, C., Herrmann, J.M., Alba, A.R.F., (2003). Effect of operating parameters on the testing of new industrial titania catalysts at solar pilot plant scale. *Applied Catalysis B: Environmental* 42 , 349–357.

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

Nogueira, R.F.P., Jardim, W.F. (1996). TiO₂ fixed bed reactor for water decontamination using solar light. *Solar Energy* Vol. 56, No. 5 , 471-477.

Noorjahan, M., Maheshwari, R. (2003). 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 , 179-187.

Padmanabhan, P.V.A., Sreekumar, J.K., Thiyagarajan, T.K., Satpute, R.U., Bhanumurthy, K., Sengupta, P., Dey, G.K., Warriar, K.G.K. (2006). Nano-crystalline titanium dioxide formed by reactive plasma synthesis. *Vacuum* 80 , 11-12.

Pelizzetti, E., Carlin, V., Minero, C., and Graetzel, M. (1991). Enhancement of the rate of Photocatalytic Degradation on TiO₂ of 2- Chlorophenol, 2,7,- Dichlorodibenodioxin and atrazine by inorganic oxidizing species. *New J.Chem.* 15, 351-359.

Pozzo, R.L., Giombi, J.L., Baltanás, M.A., Cassano A.E. (2000). *Catalysis Today* 62 (2000) 175–187.

Radjenović, J., Sirtori, C., Petrović, M., Barceló, D., Malato, M. (2009). Solar photocatalytic degradation of persistent pharmaceuticals at pilot-scale: kinetics and characterization of major intermediate products. *Applied Catalysis. B: Environmental.* 89 , 255-264.

Raloff, J. (1998). Drugged Waters: Does it matter that pharmaceuticals are turning up in water supplies. *Science News* 153, 187-189.

Rao, K.V.S., Rachel, A., Subrahmanyam, M., Boule, P. (2003). Immobilization of TiO₂ on

pumice stone for the photocatalytic degradation of dyes and dye industry pollutants . Applied Catalysis B: Environmental 46 , 77–85.

Rao, N.N., Chaturvedi, V., Puma, G.L. (2012). Novel pebble bed photocatalytic reactor for solar treatment of textile wastewater. Chemical Engineering Journal 184 , 90– 97.

Rao, P.S. and Hayon, E. (1974). Redox Potentials of Free Radicals. IV. Superoxide and Hydroperoxy Radicals. Pioneering Research Laboratory, U. S. Army Natick Laboratories, Natick, Massachusetts 01760.

Rizzuti, L., Yue, P.L.(1983). The measurement of light transmission through an irradiated fluidised bed . Chemical Engineering Science. Vol 38, 8, 1241-1249.

Roselin, L.S., Rajarajeswari, G.R., Selvin R., Sadasivam, V., Sivasankar, B., Rengaraj, K. (2002). Sunlight/ZnO-mediated photocatalytic degradation of Reactive Red-22 using thin film flat bed flow photoreactor. Solar Energy Vol. 73, No. 4 , 281–285.

Sannino, D., Vaiano, V., Ciambelli, P., Pierre, E., Eric, M.G. (2011). Avoiding the deactivation of sulphated MoOx/TiO₂ catalysts in the photocatalytic cyclohexane oxidative dehydrogenation by a fluidized bed photoreactor. Applied Catalysis A: General 394 , 71–78.

Sarria, V. K. (2003). An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants. Journal of Photochemistry and Photobiology A: Chemistry 159 , 89–99.

Si, C., Zhou, J., Gao, H., Liu, G. (2012). Photocatalytic degradation of formaldehyde in a fluidized bed with sound-magnetic assistance. Advanced Powder Technology, Vol 24, No.1 , 295-300

Smith, Z. (2001). Advanced technologies in water and wastewater treatment. In can. Journal Civil Engineering Vol 28, 49-65.

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.

Toor, A.P., Verma, A., Singh, V, Jotshi, C.K., Bajpai, P.K. (2007). Treatment of bleaching effluent from pulp and paper Industry by Photocatalytic Oxidation, TAPPI, June.

Vega, A.A., Imoberdorf, G.E., Mohseni, M. (2011). Photocatalytic degradation of 2,4-dichlorophenoxyacetic acid in a fluidized bed photoreactor with composite template-free TiO₂ photocatalyst. Applied Catalysis A: General 405 , 120– 128.

Vorontsov A.V., Evgueni, V., Savinov, N., Smirniotis P.G.,(2000). Vibro fluidized- and fixed-bed photocatalytic reactors: case of gaseous acetone photooxidation. *Chemical Engineering Science* 55 , 5089-5098.

Yang, H., Cheng, H. (2007). Controlling nitrite level in drinking water by chlorination and chloramination. *Separation Purification Technology* 56 , 392-396.

Zayani, G., Bousselmi, L., Mhenni, F., Ghrabi, A. (2009). Solar photocatalytic degradation of commercial textile azo dyes: Performance of pilot plant scale thin film fixed-bed reactor. *Desalination* 246, 344–352.

Zuccato, E., Calamari, D., Natangelo, M., Fanelli, R. (2000). Presence of therapeutic drugs in the environment. *Lancet*.355 (9217), 1789 – 1790 .