DECOMPOSITION OF COMMERCIAL AVAILABLE MONOCROTOPHOS IN AQEOUS SOLUTION OF TIO_2 BY SONOPHOTOCATALYSIS

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By

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DECLARATION

Date: _____

I hereby declare that the work embodied in dissertation entitled **"Decomposition of commercial available monocrotophos in aqueous solution of Tio_2 by sonophotocatalysis"**is original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

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CERTIFICATE

This is to certify that the dissertation entitled, "**Decomposition of commercial available monocrotophos in aqueous solution of TiO_2 by sonophotocatalysis**", is an authentic work carried out by Varun Agarwal student of M.Tech. (Environment Science and Tech.) Thapar University, Patiala, during the year 2011-2012, in partial fulfilments for the award of the Degree of Master of Technology and that the dissertation has not formed the basis for the award previously of any degree, associateship, fellowship or any other similar title to any other university or institute.

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TABLE OF CONTENTS

CONTENTS **PAGE NO.**

ACKNOWLEDGEMENT

ABSTRACT

CHAPTER1(A) INTRODUCTION **01-04**

1.1 Overview…… 01-01

1.2 Water pollution…….02-02

1.3 Problematic of water pollution…….....02-03

1.4 Waste water treatment processes……..03-03

1.5 Emerging Technologies……03-04

CHAPTER- 2(A) PESTICIDES AND THEIR EFFECT……...05-09

2.1 Overview……...05-07

2.2 Pesticides pollution……...07-09

CHAPTER- 2(B) PESTICIDE SELECTED FOR STUDY……...10-13

2.3 Overview……..10-11

2.4 Use of Monocrotophos in india……...11-11

2.5 Toxicological effects of Monorcrotophos…….11-12

2.6 Who study on Monocrotphos pesticide poisoning data in india…….. 12-12

2.7 Compatible treatment processes for hazardous compounds……..12-13

CHAPTER- 3 SONOPHOTOCATALYTIC TREATMENT……..14-24

3.1 Overview……14-14

3.2 Ultrasonic cavitation / Sonication……14-17

3.3 Photo catalysis……...17-23

3.4 Beneficial effects of Sonophotocatalytic…….23-24

OBJECTIVE OF PERSENT STUDY……25-25

CHAPTER-4 REVIEW OF LITERATURE……..26-33

CHAPTER-5 MATERIALS AND METHODS……34-39

5.1 Regents and chemicals used……34-34

5.2 Instruments used…….34-38

5.2.1) pH Meter……34-35

5.2.2) Spectrophotometer……35-35

5.2.3) COD digester…….36-36

5.2.4) Photocatalytic Reactor……..36-36

5.2.5) Ultrasonic Bath……..37-37

5.2.6) Sonophotocatalytic Reactor……..37-37

5.3) Method……..38-39

5.3.1) Preparation of Sample……38-38

5.3.2) Characterization of Pesticides……38-38

5.4) Experimental Setup……...38-39

5.4.1) Procedure……38-39

5.4.2) Analytic method……..39-39

CHAPTER-6 RESULTS AND DISSCUSSIONS……40-55

6.1) Compound Characteristics…….40-40

6.2) Absorption spectra of Commerical available Monocrotophos pesticides……..40-41

6.3) Standard curve of Commerical available Monocrotophos pesticides…….41-41

6.4) Preliminary Studies…….42-42

6.4.1) Dark Studies (Adsorption) and Photolysis studies…….42-42

6.5) Photo catalytic Treatment and Process Optimization……43-48

6.5.1) Effect of Tio_2 (Catalyst) Concentration……...43-44

6.5.2) Effect of pH……...44-45

6.5.3) Effect of strong oxidant (H_2O_2)…….45-46

6.5.4) Effect of Initial concentration of monocrotophos……...47-47

6.6) Comparivtely study between UV light and sun light for the degradation of monocrotophos…….48-48

6.7) Preliminary Studies of Ultrasonication……48-49

6.7.1) Sonolytic (US) and Sonocatalytic treatment (US+TiO_2)……..49-50

6.8) Sonophotocatalytic (UV+US+TiO_2+H_20_2) treatment……..50-50

6.9) Comparisons of Sonolysis , Photocatalytic and Sonophotocatalytic treatment….50-51
6.10) Mineralization Studies……51-53
6.10.1) COD analysis…….51-52
6.10.2) Measurement of Phosphate ions concentration……...52-53
6.11) Synergic effect……..53-54
6.12) Absorbance spectra after Sonophotocatalytic treatment……....54-54
CHAPTER-7 CONCLUSION……....55-56
CHAPTER- 8 REFERENCES……57-61

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE NO.
Figure 1.1	Water Distribution on the earth	01
Figure 2.1	Pesticides spray in Agricultural field	05
Figure 2.2	Pesticides- Classification by use	06
Figure 2.3	Use of pesticides (Global Pesticide Use 2001 (%)	07
Figure 2.4	Origin, Transport and Fate of Pesticides in Environment	08
Figure 2.5	Structure of Monocrotophos	10
Figure 3.1	Cavitation and Implosion phenomena	16
Figure 3.2	The Principle of Photocatalysis	19
Figure 5.1	pH meter	35

Figure 5.2	Spectrophotometer	35
Figure 5.3	COD digester	36
Figure 5.4	Immersion well reactor	36
Figure 5.5	UV bulb 125 watt	36
Figure 5.6	Ultrasonic Bath	37
Figure 5.7	Sonophotocatalytic Reactor	37
Figure 6.1	Absorption spectra of commercial grade monocrotophos pesticides	40
Figure 6.2	Standard curve of Commerical available Monocrotophos pesticides	40
Figure 6.3	Decrease in pollutant concentration due to adsorption and photolysis phenomena	42
Figure 6.4	Effect of Tio_2 on rate constant	44
Figure 6.5	Effect of pH on rate constant	45
Figure 6.6	Effect of H_2O_2 on rate constant	46
Figure 6.7	Effect of MCP initial concentration on rate constant	47
Figure 6.8	Effect of UV/Solar light on photo catalytic degradation of compound	48
Figure 6.9	Degradation rate due to Sonolytic(US) and Sonocatalytic(US+Tio_2) and Sonocatalytic + oxidant processes(US+Tio_2+H_20_2)	49
Figure 6.10	Effect of sonophotocatalytic degradation monocrotophos at the optimum condition of photocatalysis	50
Figure 6.11	% Degradation rate due to Sonolytic(US) and Photocatalytic(UV+Tio_2) and Sonophotocatalytic(US+UV+Tio_2+H_20_2)	51

Figure 6.12	% Reduction in COD using various processes	52
Figure 6.13	Measurment of removed phosphate ion concentration	53
Figure 6.14	Absorption spectra after Sonophotocatalytic treatment	55

LIST OF TABLES

TABLE NO.	TITLE	PAGE NO.
Table -2.1	Reported state-wise use of monocrotophos, 2001 to 2006	11
Table-3.1	Advantages of Sonication	17
Table-3.2	Oxidizing agent and their electrchemical oxidation potential	20
Table-3.3	Several and different organic compounds removed or degraded by means using of photocatalysis	22
Table-6.1	Characteristics of Commercial Monocrotophos	40

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ABSTRACT

Environmental Protection Agency (E.P.A.,1990) estimates aboutmore than 600 million pounds of pesticides enter the environment each year in the environment. Pesticides are included in a broad range of organic micro pollutants that have ecological impacts. Different categories of pesticides have different types of effects on living organisms and these different type of pesticides has a property of bioaccumulation in the environment. Mainly pesticides are not completely degraded during conventional treatment technology due to low biodegradability. Field surveys shows that due to not complete mineralization, some amount of pesticides are released in aquatic environment and mix into ground water and used as a source of drinking water. So there is a clear need to set up the emerging alternative technologies that can deal with highly concentrated and toxic nonbiodegradable pesticides.

So recently considerable interest has been shown by researchers towards the degradation of pesticides by advanced oxidation process such as photocatalysis, sonolysis, sonophotocatalysis,. These technique are basically very ecofriendly and time consuming technology and most basic advantage of these technology is completely destruction of any toxic compounds into nontoxic ending products and it can be easily carried out at room temperature and atmospheric pressure.

Basic principle behind of these technology is production of OH^{o} radical which has high oxidation potential and mainly its nonselective property. These OH^{o} radical can easily react with the toxic compound due to its high potential capability and change into nontoxic ending products.

Photocatalysis itself is a very advance technique which has large potential for the degradation of any complex organic matter. But if the two modes of irradiations (photocatalysis and sonolysis) are used in combination, degradation would be enhance because sonolysis process improve the mass transfer and surface area.

In this present work, we are investigating the sonophotocatalytic degradation of commercially used pesticide Monocrotophos. Titanium dioxide (TiO_2) was used as Photocatalyst. Experiments were performed in slurry mode in UV light and at optimized condition. The process is optimized by varying different parameters like catalyst concentration, operating pH, H_2O_2 conc., Initial pollutant conc. in photocatalytic experiment

In photocatalytic experiment, 92% degradation was found under the optimized catalyst concentration of $1gL^{-1}$, pH 4 and oxidant concentration of $0.375mgL^{-1}$ within 2 hoursand 80% mineralization was achieved in 6 hours.

In sonophotocatalytic experiment, 97 % degradation was found under same optimized condition after running of 2 hours and 88% mineralization was achieved in 6 hours.

Positive result of the synergy effect shows that combined effect has more valuable in comparison of both individuals treatment. So the results of Sonophotocatalytic degradation of monocrotophos compound showed that it could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants

CHAPTER- 1
INTRODUCTION

1.1 OVERVIEW

Water is the most abundant compound on Earth's surface, covering about 70 % of the planet. In nature, water exists in liquid, solid, and gaseous states, Total water on the earth is mainly distributed in oceans water (96.5%) and fresh water (2.5%), ground water saline (0.93%) (Figure 1.1).The Earth is often referred to as the "blue planet" because when viewed from space it appears blue. This blue color is caused by reflection from the oceans which cover roughly 71% of the area of the Earth.

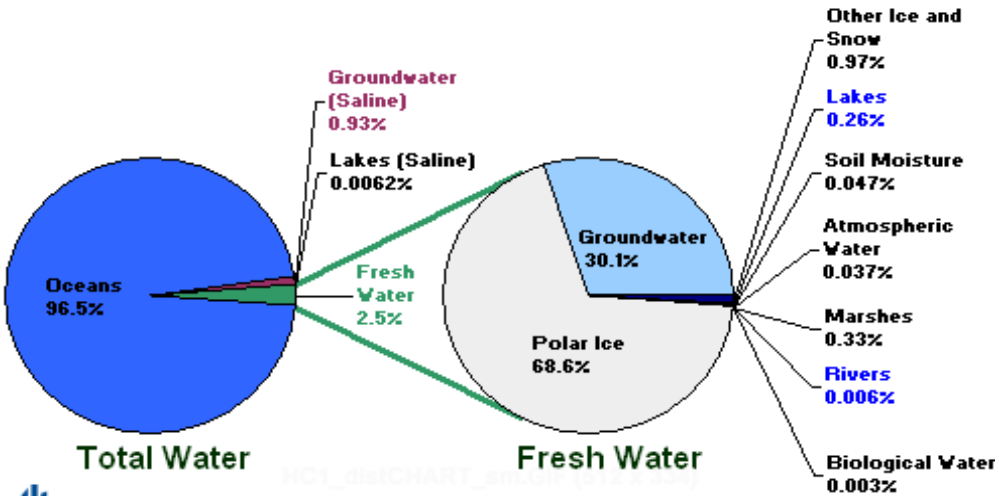

Figure 1.1 Water Distribution on the earth

1.2 WATER POLLUTION

Water pollution can be caused two sources: Point Sources and Non Point sources.

Point sources include factories, wastewater treatment facilities, septic systems, and other sources that are clearly discharging pollutants into water sources. Non-point sources are more difficult to identify, because they cannot be traced back to a particular location. Non-point sources include runoff including sediment, fertilizer, chemicals and animal wastes from farms, fields, construction sites and mines. Landfills can also be a non-point source of pollution, if substances leach from the landfill into water supplies.

The domestic, industrial, agricultural practices pollute the water. The important classes of this water pollutant are organic, inorganic, heavy metals. Some of substances like pesticides, pharam compound, dyes, etc move into bodies of organism these substances accumulate into the body of organism, Pesticides in drinking water ultimately reach humans and are known to cause various health problems..

1.3 PROBLEMATIC OF WATER POLLUTION

Water pollution has always been a major problem to the environment with industrialization in major areas and urban cities growing the water around them just keeps getting polluted. Around 80 percent of ocean pollution enters our seas from the land. Virtually any human activity can have an effect on the quality of our water environment. When farmers fertilize the fields, the chemicals they use are gradually washed by rain into the groundwater or surface waters nearby. Sometimes the causes of water pollution are quite surprising. Chemicals released by smokestacks (chimneys) can enter the atmosphere and then fall back to earth as rain, entering seas, rivers, and lakes and causing water pollution. That's called atmospheric deposition.

Pollutants can also seep down and affect the groundwater deposits. Due to this, pollutants enter groundwater, rivers, and other water bodies. Such water, which ultimately ends up in our households, is often highly contaminated and carries disease-causing microbes.

Ground water can be contaminated through various sources and some of these are mentioned below.

1. **Pesticides**. Run-off from farms, backyards, and golf courses contain pesticides such as DDT that in turn contaminate the water. Its effects on the ecosystems and health are endocrine and reproductive damage in wildlife. Groundwater is susceptible to contamination, as pesticides are mobile in the soil.

2. **Sewage**. Untreated or inadequately treated municipal sewage is a major source of groundwater and surface water pollution in the developing countries. The organic material that is discharged with municipal waste into the watercourses uses substantial oxygen for biological degradation thereby upsetting the ecological balance of rivers and lakes. Sewage also carries microbial pathogens that are the cause of the spread of disease.

3. **Nutrients.** Domestic waste water, agricultural run-off, and industrial effluents contain phosphorus and nitrogen, fertilizer run-off, manure from livestock operations, which increase the level of nutrients in water bodies and can cause eutrophication in the lakes and rivers and continue on to the coastal areas.

1.4 WASTE WATER TREATMENT PROCESSES

In order to achieve different levels of contaminant removal, individual waste-water treatment procedures are combined into a variety of systems, classified as primary, secondary, and tertiary

But the use of conventional water and wastewater treatment processes become increasingly challenged with the identification of more and more contaminates, rapid growth of population and industrial activities and diminishing availability of water resources.

The major drawback of conventional methods is not able to treat toxic, non-biodegradable organic pollutants So advance oxidation techniques have emerged in the past few years, in particularly for industrial waste water.

1.5 EMERGING TECHNOLOGIES

The emerging wastewater treatments methods like advanced oxidation processes are increasingly gaining popularity since they have shown the potential of converting harmful organic pollutants into innocuous compounds such as carbon dioxide and water. The emerging treatment technologies have been already demonstrated to successfully remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes **(Paradowska M.A, 2004).**

The major advantage of this technology is that it can completely or partially destroy organics at ambient temperature by converting them into various harmless intermediates and end products, such as carboxylic acids, carbon dioxide and halide ions. The major oxidants of AOP are hydroxyl radicals and ozone which can react with organic compounds at very high reaction rates.

CHAPTER- 2(A)
PESTICIDES AND THEIR EFFECT

2.1 OVERVIEW

Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. A large number of pesticides and insecticides are currently in use worldwide for agricultural and non-agricultural activities for several of benefit (Figure 2.1) .These include crop protection, preservation of food and materials and prevention of vector-borne diseases etc. At present, India is the largest producer and consumer of pesticides in Asia and ranks twelfth in the world for the use of pesticides with an annual production of 90,000 tons (Abhilash P.C, 2008). A vast majority of the population in India (56.7 percent) are engaged in agriculture and are therefore exposed to the pesticides used in agriculture (Randhawa G.K.1999).

Figure 2.1: **Pesticides spray in Agricultural field (Excessive use)**

Due to their wide use, they have become the second largest contaminant in drinking water and in food. Because over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments, and food (Miller, 2004). Depending on the usage of pesticides, the pesticides classification (figure 2.2) into herbicides, insecticides, micro-biocides, fungicides, nematicides (Madhavana J.et al.,2010).

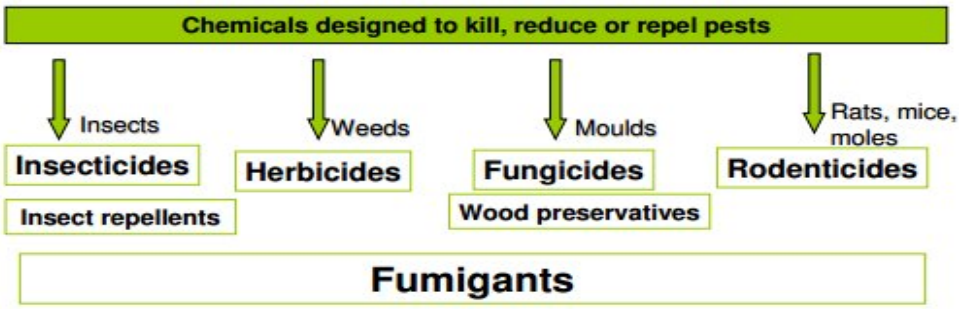

Figure 2.2 : Pesticides- Classification by use

There is a large variety of pesticides designed to kill specific pests – those most widely used are listed below

TYPE OF PESTICDES

- **Insecticides :** They are used for killing the insects (eg. Organochlorines, Organophosphates and Carbamates).This category also includes insect repellents such as diethyltoluamide (DEET) and citronella (of natural origin).

- **Herbicides :** Selective herbicides kill specific targets while leaving the desired crop relatively unharmed .They are weedkillers (e.g. Paraquat, Glyphosate and Propanil).

- **Fungicides :** Fungicides are chemical compounds used to prevent the spread of fungi or plants in gardens and crops, which can cause serious damage resulting in loss of yield and thus profit. Fungicides are also used to fight fungal infections (eg. Thiocarbamates, Dithiocarbamates).

- **Rodenticides :**They are use to kill mice, rats, moles and other rodents.Rodenticides are a category of pest control chemicals intended to kill rodents.Rodents are difficult to kill with poisons because their feeding habits reflect their place as scavengers (eg. Warfarines Indanodiones).

- **Fumigants :** They are pesticides that exist as a gas or a vapour at room temperature and may be used as insecticides, fungicides or rodenticides, especially in closed storage places. They are

extremely toxic, due to their physical properties, rapid environmental dissemination and human or animal absorption (eg. Cyanide, aluminium phosphate and Methyl bromide).

Insecticides are mostly used in developing countries and fungicides/herbicides in developed countries. Different types pesticides are using at the global level according to their usage(Figure 2.3).

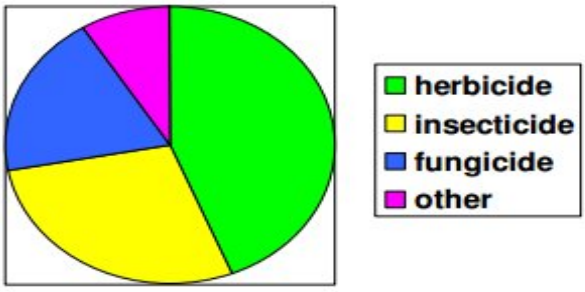

Figure 2.3 : Use of pesticides (Global Pesticide Use 2001 (%)

2.2 PESTICIDES POLLUTION

Pesticides being used in agricultural are released into the environment and come into human contact directly or indirectly. Pesticides have different distribution and persistence patterns in the environment, mainly all of them are distributed in some way through air, soil and water. Figure 2.4 illustrates the routes of pesticides (spray, granulate or seed treatment) that is applied to a given site, representing a risk to applicators, human being and wildlife.

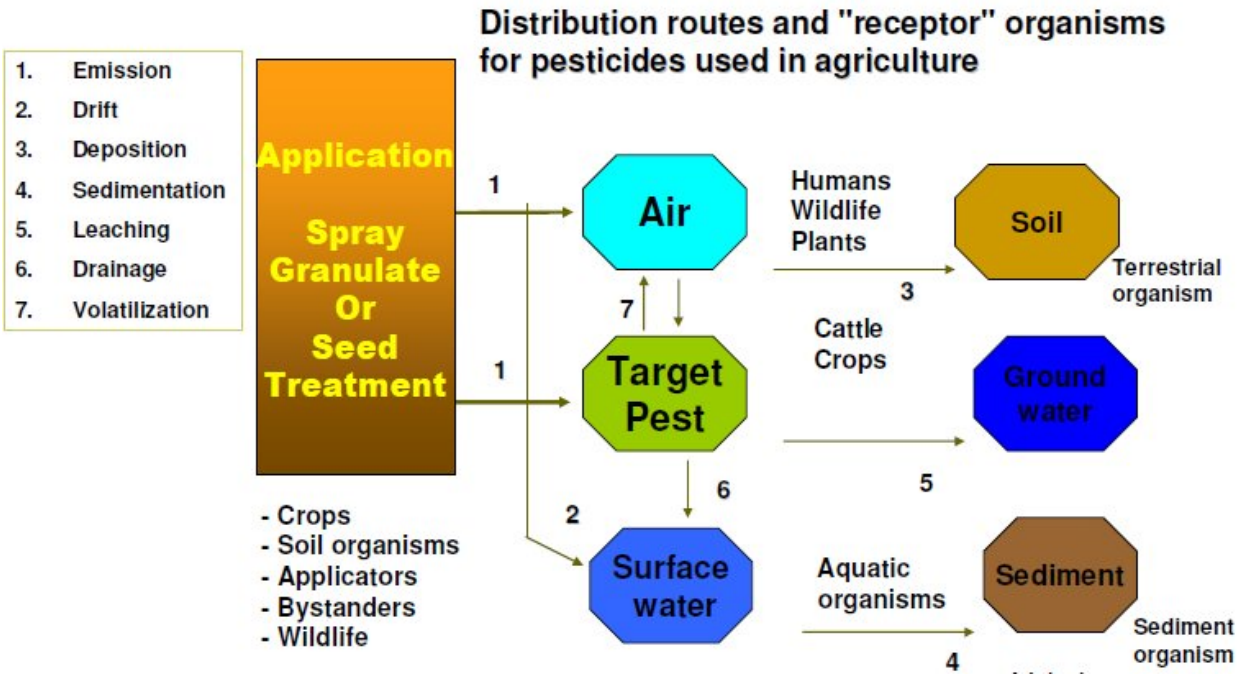

Figure 2.4 Origin, Transport and Fate of Pesticides in Environment

When a pesticide is applied directly to a target pest (plant or animal) the whole site is affected including crop plants, soil organisms and, potentially, humans and wildlife in the immediate area. In addition, part of it goes to the air or to surface waters, due to emission (1) or drift (2). Once on the target site, the pesticide may "drain"(6) into surface waters or volatilize (7) into the air. From the air it may deposit (3) on humans, wildlife or plants or on the soil. From the animals or plants where it was applied the pesticide may leak (5) into groundwater.

Pesticides in surface water may go into aquatic organisms, and by sedimentation (4) into other organisms that remain in the sediment. The persistence of the pesticide depends on its physical and chemical properties (partition coefficients, degradation rates, deposition rates) and the characteristics of the environment.

Exposing of pesticide in environment create acute and chronic effect to human being.

➢ **Chronic effect:** These effects are low-level effect and develop slowly due to long and continuous exposure to low concentration of hazardous substances. Mainly chronic effect on human being are listed below

- Abnormal growth and development

- Impaired neurobehavioral development / functions
- Cancer
- Increased susceptibility to infections
- Immunotoxicity (Eskenazi et al., 2001)

➢ **Acute effect :** These effect develop very rapidly and lead quickly to a health crisis due to exposure to a harmful substances substance on human being. Main acute effect is neurotoxicity and Endocrine disruption.

In Endocrine disruption, low doses of certain pesticides may mimic or block hormones or trigger inappropriate hormone activity Endocrine disruption may alter development and reproduction and induce birth defects (Baskin et al., 1999).

Apart from that many other type of disease are also produced in human being due such as

- Irritability
- Irreversible cholinesterase inhibition
- Cholinergic crisis:
- Nausea, vomiting
- Miosis

CHAPTER- 2(B)

PESTICIDE SELECTED FOR STUDY

Based on the field survey and literature search, the Monocrotophos was selected for the present study. The commercial grade of the pesticide was procured from the local market.

2.3 OVERVIEW

Monocrotophos is one of the highly hazardous **organophosphate insecticides** (figure2.5) that is widely used and easily available in India. It has been in use in Australia and other countries for nearly 30 years. It controls pests on a variety of crops, such as cotton, rice, and sugarcane. It is used to control a wide spectrum of chewing and sucking insects and also mites.It is acutely toxic to birds and humans, and widespread bird kills, especially of Swainson's Hawks (Fang L., 2000). Monocrotophos can be absorbed through ingestion, inhalation and skin contact. When inhaled, it affects the respiratory system.

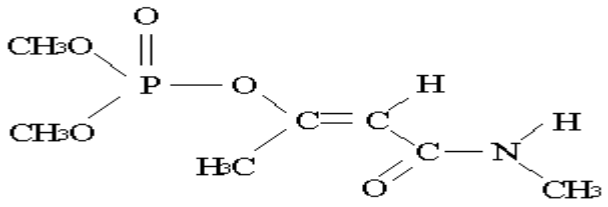

Figure 2.5: Structure of Monocrotophos

Physical and Chemical Property of Monorcrotophos

Pure monocrotophos is in the form of colourless crystals. It is soluble in water, acetone, and aliphatic alcohols, but only slightly soluble in mineral oils. Monocrotophos is fairly resistant to hydrolysis.

- **Appearance:** Monocrotophos is a reddish brown crystalline solid with a mild odor .
- **Molecular formula:** $C_7H_{14}NO_5P$
- **Chemical Name:** dimethyl (E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate
- **Molecular Weight:** 223.2(Gram/mol)
- **Melting Point:** 54-55°c

- **Solubility in water (20 °C) :** 1 kg/litre
- **Vapour pressure (20 °C)** :0.29 mPa

2.4) USE OF MONOCROTOPHOS IN INDIA

In India, monocrotophos while mainly applied against cotton pests, it is also used on rice, castor, citrus, olives, rice, maize, sorghum, sugar cane, sugar beet, peanuts, potatoes, soybeans, cabbage, onion and pepper ornamentals and tobacco. Farmers in small-holder cultivation tend to use the same insecticide for all the companion crops. Reported monocrotophos consumption data from 2001 to 2006 is provided in Table 2.1

State	Consumption (metric tons)					
Year	2001	2002	2003	2004	2005	2006
Andhra Pradesh	3 537	3 205	3 095	2 984	2 881	2 779
Bihar	131	119	115	111	107	103
Gujarat	1 101	998	963	929	897	865
Haryana	1 048	950	917	884	854	823
Karnataka	833	755	729	703	679	654
Kerala	131	119	115	111	107	103
Madhya Pradesh	760	689	665	641	619	597
Maharashtra	1 428	1 294	1 250	1 205	1 163	1 122
Punjab	1 622	1 470	1 419	1 369	1 321	1 274
Rajasthan	652	591	571	550	531	512
Tamil Nadu	665	603	582	561	542	522
Uttar Pradesh	182	165	159	154	148	143
West Bengal	215	195	188	181	175	169
ALL INDIA	**16 000**	**14 500**	**14 000**	**13 500**	**13 000**	**11 700**

Table : 2.1 Reported state-wise use of monocrotophos, 2001 to 2006 (Ministry of Agriculture, India, 2007)

2.5 TOXICOLOGICAL EFFECTS OF MONORCROTOPHOS

Monorcrotophos are well known for their bioaccumulation and neurotoxic property, because they are acting on the enzyme acetyl cholinesterase. Organophosphate pesticides irreversibly inactivate acetylcholinesterase, which is essential to nerve function in insects, humans, and many other animals. So they have full potential for neurotoxicity.

- **Acute Toxicity:** Monocrotophos, is a direct acting cholinesterase inhibitor capable of penetration through the skin. Symptoms of monocrotophos poisoning are similar to those of other organophosphate compounds. Its cholinesterase inhibiting activity causes nervous system effects. Other effect are muscular weakness, blurred vision, profuse perspiration, confusion, vomiting, pain, and small pupils. There is a risk of death due to respiratory failure. In child stage many abnormal condition are also generate by the exposing of monocrotophos.

- **Effects on Aquatic Organisms:** Monocrotophos is moderately toxic to fish. Monocrotophos causes reproductive damage to crustaceans exposed for long periods of time.

- **Effects on Other Animals (Nontarget species):** Monocrotophos is highly toxic to bees . It may also kill non-target birds which eat insects poisoned with monocrotophos.

2.6) WHO STUDY ON MONOCROTPHOS PESTICIDE POISONING DATA IN INDIA

A WHO sponsored study carried out in India showed data collected from July 1999 to June 2000 from hospitals in Andhra Pradesh, Haryana, Punjab and Karnataka and one Poison Information Centre in Ahmedabad, Gujarat. A total of 1531 cases of pesticide poisoning were recorded during this one-year period. Out of the 1531 cases, 609 were due to organophosphorus pesticides. Monocrotophos was involved in 86 cases, the largest number of poisonings due to an insecticide (World Health Organization,2009).

In one of the study, The effect of monocrotophos on brain AChE(acetyl cholinesterase), red blood cell AChE (acetyl cholinesterase), and serum ChE(cholinesterase) activity was observed in rats. Inhibition of brain AChe (87%), red blood cell AChE (72%), and serum ChE (80%) activity was observed 2 hours after treatment with a single oral dose of 3 mg/kg bw (Potrepka R.F,1999).

2.7 COMPATIBLE TREATMENT PROCESSES FOR HAZARDOUS COMPOUNDS

In general, the numerous unit operations and processes to remove wastewater contaminants are grouped together to provide various levels of treatment.

The treatment of water is divided into 3 parts:

1. **Physical** - primary methods are referred to physical or physical-chemical unit Operations. e.g. filtration, adsorption, air flotation, flocculation and sedimentation.
2. **Biological** - secondary referred to biological operations. e.g. aerobic, anaerobic and activated sludge.
3. **Chemical** - advanced or tertiary referred to chemical or to combinations of all three e.g. Thermal oxidation (combustion), Chemical oxidation, Ion exchange, Chemical precipitation, incineration.
The use of conventional water and wastewater treatment processes becomes increasingly challenged with the hazardous compounds . (Zhou. H and Smith D.W., 2001)

The actual state performance of conventional methods is clearly not suitable to treat toxic, non-biodegradable organic pollutants and new improved treatments have to be developed and tested.

To overcome the inconveniences of conventional treatment methods, **Advanced Oxidation Techniques (AOP's)** have emerged in the last decades, in particular for the treatment of pesticides. These technique are basically very ecofriendly and time consuming technology and most basic advantage of these technology is completely destruction of any toxic compounds
into nontoxic ending products and it can be easily carried out at room temperature and atmospheric pressure. AOP's differ from the other treatments processes because wastewater compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated, there is no need to dispose of materials **(Metcalf and Eddy, 2003).**

Basic principle behind of this technology is production of OHº radical which has high oxidation potential and mainly its non-selective property. These OHº radicals can easily react with the toxic compound due to its high potential capability and change into nontoxic ending products.

Sonophotocatalytic treatment is one of type of **Advanced oxidation treatment** Technique which can degrade of commercial available monocrotophos very efficiently

CHAPTER- 3

SONOPHOTOCATALYTIC TREATMENT

3.1 OVERVIEW

Sonophotocatalytic Treatment is the combination of two advanced oxidation processes i.e. ***sonication and photocatalysis***(Chen.W.S.,2011).The basic reaction mechanism for both ultrasound initiated degradation process as well as photocatalytic oxidation (either using UV light or solar energy) is the generation of free radicals and subsequent attack by these on the pollutant organic species. If the two modes of irradiations (UV and ultrasound) are operated in combination, more number of free radicals will be available for the reaction thereby increasing the rates of reaction. Also in the case of photocatalytic oxidation, the most common problem associated is the reduced efficiency of photocatalyst with continuous operation possibly due to the adsorption of contaminants at the surface and blocking of the UV activated sites, which makes them unavailable for the destruction. Moreover photocatalytic oxidation technique is also affected by severe mass transfer limitations especially in the case of immobilized catalyst type of reactors, which are generally preferred over slurry reactors to avoid solid catalyst separation problems. The turbulence induced by the cavitation phenomena can aid in eliminating the drawbacks associated with photocatalytic oxidation.

3.2 ULTRASONIC CAVITATION / SONICATION

This technique is one type of advanced oxidation technique and further it comes under **EMERGING TECHNOLOGY** of **ADVANCED OXIDATION PROCESS**.

Ultrasound is the term used to describe sound energy at frequencies above the range that is normally audible to human beings (i.e.>16 kHz). At its upper limit ultrasound is not well defined but is generally considered as 5MHz in gases and 500MHz in liquids and solids which are subdivided to reflect applications. The range 20 to 100 kHz (though in certain cases up to 1 MHz) is designates as the power ultrasound reason, while the frequencies up to 1 MHz are known as high frequencies or diagnostics frequencies (Amarnath R.K.,1998**).** Sound is composed from longitudinal waves comprising rarefactions (negative pressures) and Compressions (positive pressures). It is these alternating cycles of compression and rarefaction that, in high power ultrasonic applications, can produce a phenomenon known as “cavitation.

Cavitation is the formation, growth and collapse of bubbles in the liquid (Ravazzini A. et al., 2002). Cavitation occurs whenever a new surface, or cavity, is created within a liquid. A cavity is any bounded volume, whether empty or containing gas or vapor, with at least part of the boundary being liquid.

The collapse of the bubbles induces localized supercritical conditions: high temperature, high pressure, electrical discharges, and plasma effects. It has been reported that the gaseous contents of a collapsing cavity reach temperatures of 5500 ^{o}C, and the liquid immediately surrounding the cavity reaches 2100 ^{o}C. The pressure was estimated to be 500 atmospheres, resulting in the formation of transient supercritical water. Thus, cavitation serves as a means of concentrating the diffuse energy of sound into micro reactors. Even though the local temperature and pressure conditions created by the cavity implosion are extreme, one can have good control over the sonochemical reactions. The intensity of cavity implosion, and hence the nature of the reaction, are controlled by such factors as acoustic frequency, acoustic intensity, bulk temperature, static pressure, and the choice of liquid or dissolved gas. The consequences of these extreme conditions are the cleavage of dissolved oxygen molecules and water molecules (into •H atoms and •OH radicals).

From the reactions of these entities (•O, •H, •OH) with each other and with H_2O and O_2 during the quick cooling phase, HO_2 • radicals and H_2O_2 are formed. In this molecular environment, organic compounds are decomposed and inorganic compounds are oxidized or reduced.

Ultrasound has been widely known to induce radical reactions. This useful property has found its applications in sonolysis of water, sonolytic degradation of aqueous organic pollutants, and sonochemical synthesis of chemicals. The underlying phenomena include cavitation, microstreaming, and localized supercritical conditions. These phenomena lead to sonolytic splitting of water as well as pyrolysis of a vaporized molecule

liquids irradiated with ultrasound can produce bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse **(**Figure 3.1). which generates very high pressures and temperatures. This process is called cavitation. The

compression of cavities when they implode in irradiated liquids is so rapid that little heat can escape from the cavity during collapse.

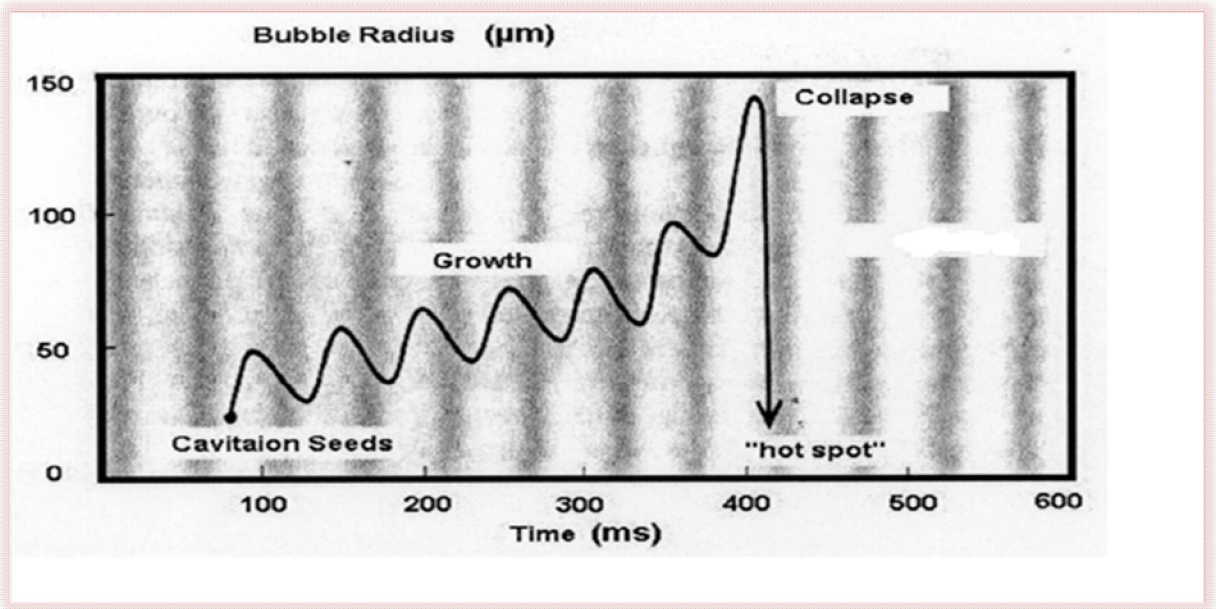

Figure 3.1 Cavitation and Implosion phenomen (Dehghani M.H and ChanganiI F., 2006)

Thus, one generates a short-lived, localized hot spot in an otherwise cold liquid. It has a temperature of roughly 5000° C (9,000° F), a pressure of about 1000 atmospheres, a lifetime considerably less than a microsecond, andheating and cooling rates above 10 billion° C per second (Dehghani M.H and ChanganiI F., 2006**).** In aqueous in phase sonolysis, there are three potential sites for Sonochemical activity, namely:

(I) The gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed through water sonolysis:

$H_2O \rightarrow H^{\cdot} + OH^{\cdot}$

(II) The bubble–liquid interface where hydroxyl radicals are localized and, therefore, radical reactions predominate although pyrolytic reactions may also occur .

(III) The liquid bulk where secondary sonochemical activity may take place mainly due to free radicals that have escaped from the interface and migrated to the liquid bulk. It should be pointed out that hydroxyl radicals can recombine yielding hydrogen peroxide which may, in turn, react with hydrogen to regenerate hydroxyl radicals:

$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$

$H_2O_2 + H^{\cdot} \rightarrow H_2O + OH^{\cdot}$ (Berberidou C. et al., 2007)

Ultrasonication process mainly remove the problems which are associated with the photocatalysis. Ultrasonication has many of advantage (Figure 3.1) due to which it is mainly come in emerging technology .

S.NO.	ADVANTAGES
1	Able to treat very toxic wastes at mild conditions.
2	Environmentally friendly technology using only electricity as a reactant.
3	The energy consumption depends on the chemical oxygen demand (COD).
4	The sono- treatment can be simply stopped by switching the power off.
5	Cost effective and safe.
6	Fully-controlled by a computer.
7	Even effluents with low conductivity can be treated.

Table-3.1 Advantages of Sonication.(Roselló I.R., 1999)

3.3 PHOTO CATALYSIS

Photocatalysis comes under the ***established technology*** of ***advanced oxidation process***

Established Technologies are of two types

A) **Homogeneous Photo catalysis** (Poon C.S. et al.,1998), (Kiwi J. et al.,1993).

B) **Heterogeneous Photo catalysis** (Elmolla S.et al.,2009)

A) HOMOGENOUS PHOTOCATALYSIS

The application of homogeneous photo degradation (single-phase system) to treat contaminated waters, concerns the use of UV/ozone and UV/H_2O_2. The use of UV light for photo degradation of pollutants can be classified into two principal areas.

(1) Direct photo degradation, which proceeds following direct excitation of the pollutant by UV light and

(2) Photo-oxidation, where light drives oxidation processes principally initiated by hydroxyl radicals.

The latter process involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. Three major oxidants used are

- Hydrogen peroxide
- Ozone
- Photo-Fenton system (fe^{3+}/H_2O_2)

B) HETEROGENEOUS PHOTOCATALYSIS

Photocatalysis or UV/TiO_2

The process is heterogeneous because there are two active phases, solid and liquid.

The word photocatalysis is composed of two parts:

1). The prefix *photo*, defined as "light",

2). *Catalysis* is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

The definition of photocatalysis is basically the acceleration of a photoreaction by the presence of a catalyst.

A more in depth approach would include that the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction (Figure 3.2).

1. Exposure to ultraviolet rays (UV) The electron jumps up from the surface when light (Ultraviolet rays) hits the photo catalyst (titanium dioxide). At this time the hole which the electron jumped up from is called the positive hole, and has worn the charge of the plus.

2. OH radical appearance The positive hole has the strong oxidation power and takes the electron from OH^- (hydroxide ion) in water. At this time OH^-, that was taken the electron, becomes OH radical of very unstable condition.

3. Decomposition of organic compound OH radical takes the electron by the strong oxidation from the nearby organic compound to become stable oneself. In this way the organic compound is decomposed by loss of the electron and finally becomes carbon dioxide and water, and emanated to an atmosphere.

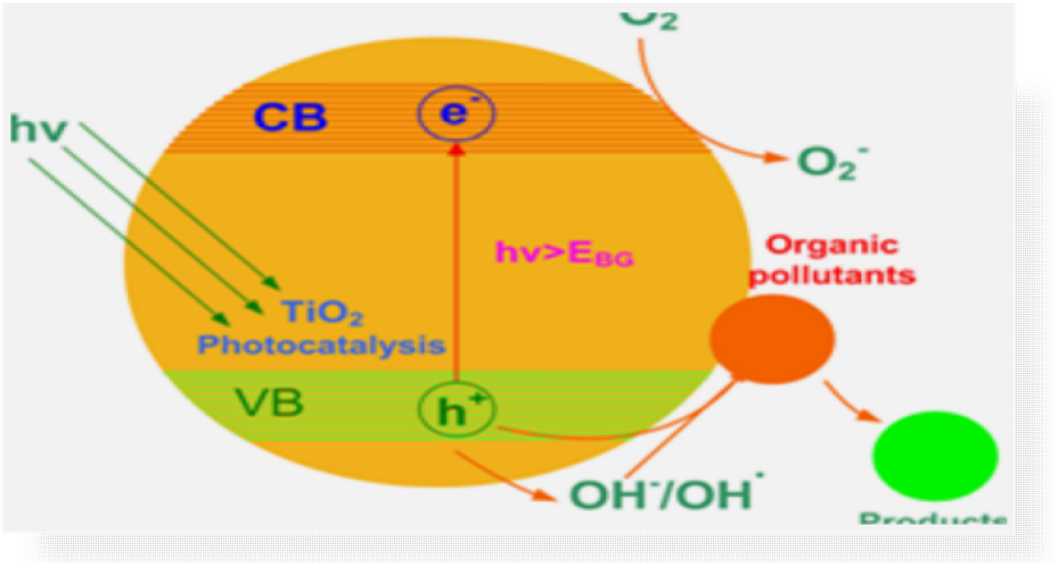

Figure 3.2 The Principle of Photocatalysis

Advanced oxidation processes typically involve the generation and use of hydroxyl radical, along with other common oxidants, that is given in the Table–3.2, with exception of fluorine ,hydroxyl radical is one of the most active oxidant **(source :Metcalf and Eddy)**

Oxidizing agent	**Electrchemical Oxidation Potential, eV**	**EOP relative to chlorine**
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30

Table-3.2 Oxidizing agent and their electrochemical oxidation potential

Hydroxyl radicals are characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment.

Following are the reactions involving in photo catalysis:-

Concerning photocatalysis with titanium dioxide as the catalyst, electrons in conduction band (e_{cb}^-) and holes in the valence band (h_{vb}^+) are produced when the catalyst is irradiated with light energy higher than its band gap energy E_{bg} ($h\nu > E_{bg}$).

1) $TiO_2 + h\nu\ (UV < 400nm) \rightarrow TiO_2\ (e_{cb}^- + h_{vb}^+)$

2) $H_{vb}^+ + H_2O \rightarrow H^+ + HO\cdot$

3) $H_{vb}^+ + HO^- \rightarrow HO\cdot$

4) Organic molecule $+h_{vb}^{+} \rightarrow$ Oxidation Products

5) $E_{cb}^{-} + O_2\,O \rightarrow O_2^{\cdot -}$

6) $O_2^{\cdot -} + H^{+} \rightarrow HO_2^{\cdot}$

7) Organic molecule $+e_{cb}^{-}$ + reduction products + Radicals ($HO^{\cdot}$, $HO_2^{\cdot}$) + organic compounds → Degradation products

Among the possible semiconductors, TiO_2, or Titanium Dioxide, (E_g = 3.2 eV) is most extensively used because it has following many advantages

ADVANTAGE OF TiO_2

1) Inert(chemically and biologically).

2) An appropriate gap b/w valence and conduction band, So easily an electron can jump from VB TO CB

3) Better from safety point of view.

4) Having low cost, limits the choice of convenient alternatives.

5) TiO_2 is of special interest as it can use natural UV.

6) Band gap energy = 3.2 eV (VB energy = 3.1 eV & CB energy = -0.1 eV)

7) Absorbs in near UV light (<387 nm) (i.e., natural (solar) energy)

Some of problems are associated with suspension form Tio_2 .Removal of catalysis after treatment is very difficult. This problem can be overcome with using of immobilized form of Tio_2.

Several and different organic compounds are susceptible to be removed or degraded by means using of photocatalysis , as in Table-3.3 (Ozencilh H., 2007).

Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, *tert*-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Dyes	Anthraquinone, diazo, monoazo
Ethers	Tetrahydrofuran

Table-3.3 Several and different organic compounds removed or degraded by means using of photocatalysis

APPLICATIONS:

1) This technique is basically used for the treatment industrial effluent and sewage sludge.

2) Destruction of cell wall and the membrane of prokaryotes are composed of complex organic materials such as peptidoglycan, teichoic acids, and complex polysaccharides, which are not readily biodegradable

3) Removal of pollutant s from dye industry and textile industry and others organic pollutants like pesticides and hazardous metals.

4) Cleaning of drinking water, as well as contaminated soil.

5) Used for the dewatering of sludge

3.4) BENEFICIAL EFFECTS OF SONOPHOTOCATALYTIC

In Sonophotocatalysis, the beneficial effect of coupling photocatalysis with sonolysis as well as adding hydrogen peroxide can be attributed to the increased production of hydroxyl radicals in the reaction system through the following steps, reactions

(i) Water sonolysis

(ii) Reaction of hydrogen peroxide with the hydrogen atoms formed from water sonolysis

(iii) Hydrogen peroxide photolytic dissociation

(iv) Reaction of hydrogen peroxide with the super oxide radical anions formed during Photocatalysis

(v) Reaction of hydrogen peroxide with conduction band electrons

1) H_2O + ultrasound → $H^{\cdot}$ + $HO^{\cdot}$

2) H_2O + ultrasound → ½ H_2 + ½ H_2O_2

3) $H_2O_2 + H^{\cdot} \rightarrow H2O + HO^{\cdot}$

4) H_2O_2 + hv → $2HO^{\cdot}$

5) $H_2O_2 + O_2^{\cdot -} \rightarrow HO^{\cdot} + HO^{-} + O_2$

There have been many studies depicting the observed synergism and the enhanced rates of degradation for the combinatorial operation of sonochemical reactors and photocatalytic oxidation

have given an extensive overview of different studies depicting the use of Sonophotocatalytic oxidation for treatment of pollutant wastewaters. It has been generally observed that the rates of degradation for the combination of ultraviolet and ultrasonic irradiation are at times order of magnitude higher as compared to individual operation.

It should be noted that in the situations where the adsorption of pollutants at the specific sites is the rate controlling step, ultrasound will play a profound role due to substantial increase in the number of active sites and also the surface area available due to defragmentation of the catalyst agglomerates under the action of turbulence generated by acoustic streaming along with an increase in the diffusion rates of the contaminants.

- Increased production of hydroxyl radicals in the reaction.
- Enhanced mass transfer of organics between the liquid phase and the catalyst surface.
- Increased catalytic activity due to ultrasound de-aggregating catalyst particles, thus increasing surface area.

OBJECTIVES OF PERSENT STUDY

Main objective of the study is to treat commercial available pesticides which cannot be completely treated by conventional treatment technologies/ biological methods employed in industry. In an attempt to increase the efficiency of degradation of the impurities present in the wastewater and to improve the economics of the treatment, the work was carried out on the degradation of commercial available monocrotophos pesticides using heterogeneous Sonophotocatalytic (Sonolysis + Photocatalysis) treatment. Combining of these two modes of irradiations i.e. US and UV eliminate the drawbacks of individual process and generate more number of hydroxyl radicals. This treatment does not transfer pollutants from one phase to another and leads to complete mineralization of organic nonbiodegradable compounds into simpler end products. The study was undertaken with the following objectives:

- To study the degradation of monocrotophos compound using photocatalytic process
- To study the effect of various parameters such as concentration of catalyst, pH, H_2O_2, Initial Concentartion on degradation rate of these compounds and their kinetic studies
- To study the degradation of model compound using Sonophotocatalytic process and calculate synergy.

CHAPTER- 4

REVIEW OF LITERATURE

The treatment of industrial wastewater before discharge to prevent the quality of natural water body from deterioration and to meet regulatory requirements continues to be a significant challenge of environmental protection. In the field of wastewater treatment, many kinds of technologies in the areas of chemistry, physics, and even biochemistry have been applied under the considerations of economics and practicability. Recently, considerable interest has been shown by researchers all over the world in the application of ultrasound to improve the performance of photocatalytic degradation of organic and inorganic contaminants in aqueous streams. The chemical effects of ultrasound enhance chemical reactivity through the phenomenon of cavitation which involves the nucleation, growth and collapse of bubbles in a liquid. Cavitation occurs whenever a new surface, or cavity, is created within a liquid. A cavity is any bounded volume, whether empty or containing gas or vapor, with at least part of the boundary being liquid. The collapse of the bubbles induces localized supercritical conditions: high temperature, high pressure, electrical discharges, and plasma effects. It has been reported that the gaseous contents of a collapsing cavity reach temperatures of 5500°C and the liquid immediately surrounding the cavity reaches 2100°C. The pressure was estimated to be 500 atmospheres, resulting in the formation of transient supercritical water. Even though the local temperature and pressure conditions created by the cavity implosion are extreme, one can have good control over the sonochemical reactions. The intensity of cavity implosion, and hence the nature of the reaction, are controlled by such factors as acoustic frequency, acoustic intensity, bulk temperature, static pressure, and the choice of liquid or dissolved gas. The consequences of these extreme conditions are the cleavage of dissolved oxygen molecules and water molecules (into •H atoms and •OH radicals). From the reactions of these entities (•O, •H, •OH) with each other and with H_2O and O_2 during the quick cooling phase, HO_2• radicals and H_2O_2 are formed. In this molecular environment, compounds are decomposed.

Many literatures show that a some of work have been done on the technical grade monocrotophos .

Sonophotocatalytic degradation of monocrotophos using TiO_2 and Fe^{3+} was studied by **Madhavan J. et al., 2010** worked on. In this study, sonolytic, photocatalytic and sonophotocatalytic degradation of MCP in the presence of homogeneous (Fe^{3+}) and heterogeneous photocatalysts

(TiO_2) was studied .Finally results concluded that, the photocatalytic degradation rate using TiO_2 was found to be lower than that of sonolysis alone due to the interference of phosphate ions formed as an intermediate product. On the other hand, a 15 fold enhancement in the degradation rate was found when photolysis was carried out in the presence of Fe^{3+} compared to the rate observed with photolysis alone. The combination of sonolysis and photocatalysis (using either TiO_2 or $Fe^{3+)}$ showed a detrimental effect. Synergy indices of 0.62 and 0.87 were found for the sonophotocatalytic degradation of MCP in the presence of TiO_2 and $Fe^{3+,}$ respectively.

Ku Y. et al., 1999 studied reaction behaviors of decomposition of monocrotophos in aqueous solution by UV and UV/O_3 processes. The decomposition of monocrotophos (*cis*-3-dimethoxyphosphinyloxy-*N*-methyl-crotonamide) in aqueous solution by UV and UV/O_3 processes was studied. The experiments were carried out under various solution pH values to investigate the decomposition efficiencies of the reactant and organic intermediates in order to determine the completeness of decomposition. Results concluded that the combination of O_3 with UV light apparently promoted the decomposition and mineralization of monocrotophos in aqueous solution. For the UV/O_3 process, the breakage of the C=C bond of monocrotophos by ozone molecules was found to occur first, followed by mineralization by hydroxyl radicals to generate CO_3^{-2}, PO_4^{-3}, and NO_3^- anions in sequence.

Anandana S.et al., 2006 worked on photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension. In this study, La-doped ZnO nanoparticles with different La contents were synthesized and characterized by various sophisticated techniques such as XRD, UV–vis, AFM, XPS, and HR-SEM. It was found that La^{3+} is uniformly
dispersed on ZnO nanoparticles in the form of small La_2O_3 cluster. The photocatalytic activity of La-doped ZnO for the degradation of MCP was studied and the results are compared with ZnO and TiO_2. It was observed that the rate of degradation of MCP over La-doped ZnO increases with increasing La loading up to 0.8 wt% and then decreases. The TOC results demonstrated that La-doped ZnO requires shorter irradiation time for the complete mineralization of MCP than pure ZnO. The relative photonic efficiencies and the photocatalytic activity of the 0.8 wt% La-doped ZnO are much higher as compared to those of pure ZnO and TiO_2. It was concluded that small particle size,

separation of charge carriers (e−/h+), rough and high porous surface of La-doped ZnO are the major constituents for its enhanced photocatalytic activity.

Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by TiO_2/Hβ was studied by **Shankar M.V.et al., 2004**. In this study, the adsorption of monocrotophos (MCP) was carried out over HY, Hβ and H-ZSM-5 zeolites. The results are shown that adsorption property of TiO_2 supported on Hβ zeolite enhances the photocatalytic degradation of MCP. Since MCP and its intermediates are adsorbed well over supported TiO_2 they are completely mineralized. The adsorption of MCP follows the order Hβ> HY > H-ZSM-5 and hence Hβ was chosen as the support for TiO_2. The photocatalytic degradation of MCP on TiO_2 and TiO_2/Hβ catalysts was studied using low-pressure mercury lamps (λ = 254 nm) in a slurry reactor. The Hβ supported TiO_2 showed higher degradation efficiency than bare TiO_2. TOC results reveal that under optimal conditions TiO_2 requires 540 min and supported TiO_2 requires less than 420 min for complete mineralization of MCP. Supported TiO_2 shows higher relative photonic efficiency for both degradation and mineralization.

Lev D. et al., 2000 investigated Sonophoto-catalytic destruction of organic contaminants (salicyclic acid) in aqueous system on TiO_2 powders. The use of ultrasound during photocatalysis had a pronounced effect on thje rate and efficiency of salicylic acid destruction as compared with UV-light photocatalysis alone. The possible reason of the increased activity under ultrasonication due to aggregate breakage and photocatalytic utilization of species produced by the ultrasound The combination of the action of ultrasonic waves and UV-assisted photocatalytic yielded synergistic effect for the catalyst with smaller particle size **a)** Aldrich anatase, **b).**Hombikal UV-100(HK), **c).**Ishihara ST-21(ST), **d).**Degussa P25.So finally they concluded that. in the Salicylic acid degradation,among the different catalyst(Aldrich P25,ST) P25 exhibited the highest activity for the degradation of salicylic acid under the UV irradiationsand also in UV+US ,under the UV,degradation rates are 0.064 mol/min.

When concentration of catalyst is 0.1g/l and increasing the concentration of catalyst .it increase and rates become 0.076mol/min.During the increasing the concentration of catalyst, degradation is 0.101mol/min under the UV and under the UV+US ,rates become 0.119mol/min.

Sonophotocatalytic degradation of congo red and methyl orange in the presence of TiO_2 as a catalyst was studied by **Nestor Javier B.P. et al., 2006**. Two types of TiO_2 catalyst were used **1)** Degussa P25, **2)** 99% anatase and they studied the effect of a number of parameters such as initial concentration of dye, the presence of dye, the presence of oxygen and ultrasound amount of TiO_2. They observed that photo catalysis oxidation rate of aqueous solutions of congo red and methyl orange shows a remarkable increase when it is carried out in the presence of ultrasound. The increase of congo red concentration produces a quenching effect on first order reaction rate for the sonophotocatalysis oxidation process. After sometimes more oxidation is occur under the sonophotocatalysis than the photocatalysis and P25 show highest catalytic activity than anatase form and finally it was shown that positive effect of ultrasound does not only occur on oxidation reactions but also on reduction reactions.

Madhvan J. et al., 2010 have worked on sonolytic, photolytic and sonophotolytic degradations of IBP in the presence of homogeneous (Fe^{+3}) and heterogeneous photocatalysis. IBP is antiflammatory drug found in aqueous environment as a pollutant due to its wide spread use .so they studied sonolytic, photolytic and sonophotocatalytic degradation of IBP in the presence of homogenous (Fe^{+3}) and heterogeneous photocatalysis (TiO_2).They observed that sonolytic degradation followed first order dependence with respect to IBP. Both Tio_2 and Fe^{+3} sonophotocatalysis showed a slight synergy in degradation of when compared with the individuals sonolysis and photocatalysis and percentage of degradation decrease with increasing initial concentration of IBP. In the presence of fe^{+3}, degradation rates increase and become 45% only under the sonolysis which take double time for same degradation in the absence of iron ions

Synergic effect of sonolysis combined with photocatalysis in the degradation of an azo dye was studied by **Elena selli, 2002** .They observed that photocatalysis and sonolysis exhibit the synergistic effects in the degradation of an azo dye .when low ultrasound frequency is employed.The degradation of azo dye in aqueous suspensions was systemically evaluated under sonolysis ,photocatalysis and sonophotocatalysis as a function of dye concentration ,amount and type of catalyst ,catalyst addition H_2O_2. The evolution of H_2O_2 was also monitored. Synergistic effect of the combination of ultrasound and photocatlsyis should mainly involve the aqueous phase

and be due to an increased concentration of reactive radicals ,consequent to the action of ultrasound on the peroxide species produced by both photocatalysis and sonolysis .

Demetrious et al.,2007 have worked on photocatalytic degradation of reactive black 5 dye in aqueous solutions and coupling with ultrasound irradiation.They investigated the degradation of reactive black is as representative dye found in textile effluents,by mean of ultrasound irradiation over TiO_2 suspensions and with their combined applications.So several TiO_2 for catalyst were used which have different charter ices **a).**Aldrich anatase **b).**Hombikal UV-100(HK) **c).**Ishihara ST-21(ST) **d).**Degussa P25 **e)** Tronox .

Than they noted that 90% decoloration is achived after 90 min. of reaction with all Tio_2 samples.But PC 500 and Aldrich which led to only about 40% and 70% decoloration respectively and COD is analyzed after the Sampling .90 min. it decrease 53% for UV 100(TiO_2 Catalyst) and 89% for P25 (TiO_2 Catalyst).
They also noted that Decoloration depends strongly on the Solution pH and is substantially Reinforced at acidic conditions ,while Hindered at alkaline conditions .The extent of RB 5 decoloration after 20 min. at pH values of 2.6,5.8,and 9 Was 97% ,49% and 6% respectively .

Tzeng T.W. et al.,2011 reported the work on Photocatalytic activity of sulfonamide antibiotic in aqueous suspension of TiO_2-P25.The results shows that the photo-degradation of SMT occurred under the irradiation of ultraviolet-C light (UVC: 254 nm) with or without TiO_2 and the presence of TiO_2 enhanced the photo-degradation rate. The degradation rate decreased with increasing the initial concentration**.** The photolytic degradation of 9 mgL^{-1} SMT was performed under UV-C irradiation for 4 hr and the results confirmed that with increasing pH, the degradation rate of SMT increased. Addition of radical scavenger revealed photocatalytic mechanisms of sulfamethazine on TiO_2 involving holes and OH radicals.

Photocatalytic activity of sulfamethoxale antibiotic in aqueous suspension of TiO_2 was studied by **Abellen M.N. et al., 2007**. The aim of this study is the evaluation of photocatalysis as a suitable process to degrade an antibiotic, the sulfamethoxazole. In this way, sulfamethoxazole in aqueous

solution was treated by using titania in suspension as catalyst, and UV light.Than results shows that degradation of sulfamethoxale depend on many factor

1) Effects of UV radiation on Sulfamethoxazole degradation

2) Presence of dissolved oxygen in the experiments

3) Influence of TiO_2 concentration.

4) Influences of pH

Sulfamethoxazole degradation and TOC reduction were improved when titania concentration was increased, until an optimum located between 0.5–1.0 g TiO_2/L.

Under the studied conditions, 82% of sulfamethoxazole degradation and 23% of TOC reduction was achieved when working with 0.5 g TiO2/L. The sulfamethoxazole degradation is not

Altered when the pH is changed, however, the TOC removal can suffer an important enhancement when the pH is varied from 2 to 11.

This effect can be probably due to the ionic nature of the intermediates in a certain pH condition, but it can also be due to the presence of the ion sulfate when the initial pH is adjusted to 2, since this anion can act as hydroxyl scavenger and can compete with the molecules for the photon of the system.

Xekoukoulotakis P. et al.,2010 reported the work on kinetics of UV-A/TiO_2 photocatalytic degradation and mineralization of the antibiotic sulfamethoxazole in aqueous matrices.In this experiments the photocatalytic degradation and mineralization of the antibiotic sulfamethoxazole (SMX) in aqueous TiO_2 suspensions was investigated UV-A irradiation was provided by a 9W lamp at a photon flux of 2.81×10−4 Einstein/min and runs were performed at SMX initial concentrations between 2.5 and 30 mg/L, six commercially available TiO_2 catalysts at loadings between 100 and 750 mg/L, acidic or near neutral conditions. The results shows that degradation of sulfamethoxazole is depend on many factor

1)Catalyst screening and activity

2) Effect of dissolved oxygen

3)Effect of SMX concentration

4) Effect of catalyst loading

Semiconductor photocatalysis based on Degussa P25 TiO_2 is an efficient method for the degradation and mineralization of sulfamethoxazole in aqueous solutions. Process performance is

affected by several factors, namely irradiation time, photocatalyst type and loading, the presence of electron acceptors and the solution pH.

Elmolla S. et al., 2009 have worked on Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. The study examined the effect of operating conditions (zinc oxide concentration, pH and irradiation time) of the UV/ZnO photocatalytic process on degradation of amoxicillin, ampicillin and cloxacillin in aqueous solution. The results shows that pH has a great effect on amoxicillin, ampicillin and cloxacillin degradation. The optimum operating conditions for complete degradation of antibiotics in an aqueous solution containing 104, 105 and 103 mg/L amoxicillin, ampicillin and cloxacillin, respectively were: zinc oxide 0.5 g/L, irradiation time 180 min and pH11.
Under optimum operating conditions, complete degradation of amoxicillin, ampicillin and cloxacillin occurred and COD and DOC removal were 23.9 and 9.7%, respectively

Wojciech B. et al., 2009 have workrd on Photocatalytic degradation of sulfa drugs with TiO_2, Fe salts and TiO_2/FeCl3 in aquatic environment—Kinetics and degradation pathway. In this experiments, the photocatalytic degradation of sulfanilamide, sulfacetamide, sulfathiazole, sulfamethoxazole and sulfadiazine in aqueous solutions was examined during their irradiation with UV-A (366 nm) with TiO_2, Fe salts and TiO_2/FeCl3 catalysts. The study was carried out by HPLC-UV, HPLC/MS-EI and total organic carbon (TOC) methods. It was found that sulfonamides undergo photocatalytic degradation in processes conducted in the presence of Fe^{+3} salts (homogeneous process) and in the presence of TiO_2-P25 and TiO_2 - RH/$FeCl_3$ (heterogeneous process). Among the salts used, the highest catalytic activity was provided by $FeCl_3$ and $Fe(NO3)_3$, while among the heterogeneous catalysts, TiO_2-P25 and TiO_2-RH/ $FeCl_3$ were most active. In processes with Fe^{+2} salts, the photocatalytic degradation of sulfonamides proceeds at a significantly slower rate. The optimum photocatalyst for degradation of sulfonamides was FeCl3 due to its high catalytic activity, low cost, non-toxicity and simplicity of the technological process. The photocatalytic process carried out in the presence of $FeCl_3$ occurred only in a narrow pH range, with a maximal rate at about pH 3. It was found that the initial concentrations of sulfonamide and $FeCl_3$ had a significant influence on the photocatalytic reaction rate.

Immobilization of TiO_2 on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants was studied by **Venkata Subba Rao K. et al., 2003.** Immobilization of TiO_2 on pumice stone is an easy and efficient method to obtain photocatalytic reactions without the problem of filtration. The fact that pumice stone is soft and only available as pellets can be eliminated by using thin-film fixed bed reactor with pellets fixed on a slanting plank. It can be used with anycommercial grade of titania. 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. It is important for long term application of photocatalysis to depollute wastewaters.

Chin Mei Ling, 2004 have worked on Performance of photocatalytic reactors using immobilized TiO2 film for the degradation of phenol and methylene blue dye present in water stream. In this experiment, TiO_2 thin film photocatalyst was successfully synthesized and immobilized on glass reactor tube using sol–gel method. The synthesized TiO_2 coating was transparent, which enabled the penetration of ultra-violet (UV) light to the catalyst surface. Two photocatalytic reactors with different operating modes were tested: (a) tubular photocatalytic reactor with re-circulation mode and (b) batch photocatalytic reactor. The results shows that, the synthetic TiO_2 thin film developed gave encouraging photocatalytic activity for decomposing organic compounds present in water and can be applied for water purification. The higher stirrer speed was required in the batch photocatalytic reactor to achieve high performance in decomposing organic compounds. The use of H_2O_2 as an oxidant in treating highly toxic chemical compounds was found to be efficient. In the tubular photocatalytic reactor, total reaction time of 11 min (5 passes), each pass with residence time of 2.2 min with re-circulation resulted in 50% MB degradation. The pH value of the solution influenced photocatalysis reaction due to the adsorption property of organic compound.

CHAPTER- 5

MATERIALS AND METHODS

Raw sample of Commercial available monocrotophos pesticides was purchased directly from market and was prepared in Distilled water at the conductivity of $25\ °C/\mu S \cdot cm^{-1}$.

5.1) Regents and chemicals used

Mainly chemicals used in all these experiment which are following

- The photo catalyst was TiO_2 P-25 (a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30, procured from Degussa Company, India branch, Bombay with a BET surface area of $50m^2g^{-1}$ and average particle size of 30 nm)
- Strong oxidant H_2O_2 (30% V/v,) was used
- COD was also performed for determining the mineralization. For COD analysis, Potassium dichromate solution (Containing Mercuric sulphate and Concentration Sulphuric acid), COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and Ferroin indicator were prepared.
- $SnCl_2$, Ammonium molybadate solution were used for orthophosphate estimation.
- H_2SO_4 (0.1N) and NaOH (0.1N) were used for adjusting the pH of sample and Distilled water was used for making the solution of sample throughout the process.

5.2) Instruments used

5.2.1) pH Meter

The pH of the solution was adjusted with the help of HCl(0.1N) and NaOH(0.1N) and measured with the help of pH meter (purchased from Eutech instrumentation, figure 5.1). pH Meter was calibrated with freshly prepared buffur solutions (of pH 4and 9) from time to time throughout study

Figure 5.1: pH meter

5.2.2) Spectrophotometer

UV-Vis (Hitachi V- 500 UV/VIS, Japan) spectrophotometer was used for degradation analysis of monocrotophos (Figure 5.2).

Figure 5.2: Spectrophotometer

5.2.3) COD digester

COD digester was used for digestion of the COD vials (Figure-5.3).

Figure-5.3: COD digester

5.2.4) Photocatalytic Reactor

This Photocatalytic Reactor (immersion well reactor) is made up of borosil glass and they are fixed volume batch reactor and having capacity 200ml (Figure-5.4).UV bulb (125 watt, Figure-5.5) is used as a light source and this reactor also have the phenomena of cooling jacket. In cooling jacket, inlet and outlet tubes is provided for water circulation.

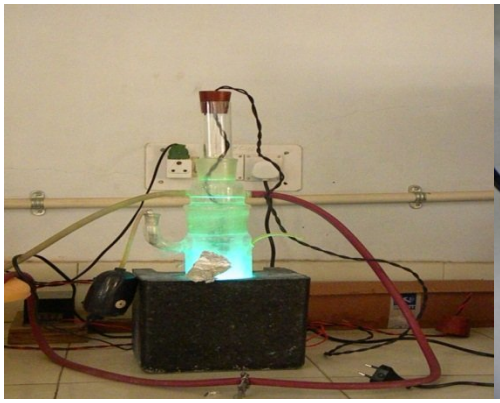

Figure-5.4 Immersion well reactor

Figure-5.5 UV bulb 125 watt

5.2.5) Ultrasonic Bath

Ultrasonic bath is used for Sonication and Ultrasonic bath Tank size is 12’’x6”x6” (H) (Figure-5.7). It creates the ultrasonic waves at the frequency of 33 KHz and its model no. is EN 60 US.

Figure-5.6 Ultrasonic Bath

5.2.6) Sonophotocatalytic Reactor

This reactor is combination of Photocatalytic Reactor and Ultrasonic Bath (Figure-5.8). Immersion well reactor is placed in the ultrasonic bath.

Figure-5.8 Sonophotocatalytic Reactor

5.3) METHOD

5.3.1) Preparation of Sample

Initially the stock solution was prepared of 200 mgL^{-1},by adding a known amount of pesticides (0.555µL) into distilled water in a 1-liter amber coloured volumetric flask to protect it from light. Commercial Monocrotophos is easily dissolved in water so there is no need to keep the solution on stirring for dissolving.

5.3.2) Characterization of Pesticides

Pesticides sample was analyzed for the COD, PO_4^{-3}, pH .The entire experimental setup was repeated to get the reproducibility of results. Parameters were analyzed by methods given in standard methods for the examination of water and wastewater 1989(17th edition) and single distilled water was used throughout the study. The methods used are follows.

Estimation of COD: COD was estimated as per the standard method no. 5220 C, page no. 5-14 from Standard Methods for the examination of water and wastewater, 1989 (17^{th} edition). Samples were digested in COD digester.

Estimation of PO_4^{-3}: Initially PO_4^{-3} ions were estimated as per standard manual of chemical and biological Methods for Seawater Analysis.

5.4) Experimental Setup

5.4.1) Procedure

All the procedures were carried out in batch process. Sample was treated in **UV, US** and **UV+US.** 200 ml of aqueous solution with the TiO_2 catalyst (in suspension form at different concentration) was added every time in photoreactor and sometimes strong oxidant (H_2O_2) was also added in reactor for generating the more amount of OHº. In some of experiments, pH was also change of compound solution by using of H_2SO_4 and NaOH. Maximum running of sample was about 5 hour (depend on experiment).

Samples were withdrawn after half hour and filtered from 0.45 micron syringe filter. For UV+US immersion well reactor was placed in the ultrasonic bath.

Results were then optimized regarding for TiO_2 concentration, pH, Oxidant concentration (H_2O_2), initial pesticides concentration. Tests were repeated for the getting the reproducibility of results.

5.4.2) Analytic method

UV-Vis spectrophotometer was used for degradation analysis of monocrotophos. Decrease in absorbance of irritated sample indicate the degradation of pesticides. One of the degradation analysis method of monocrotophos was determining by removal of PO_4^{-3} ions concentration through the degradation of monocrotophos. Percentage removal of phosphate ions indicated the degradation of pesticides. The determination of PO_4^{-3} ions was performed by ammonium molybadenum method. COD test was also performed for the determining the mineralization of monocrotophos.

CHAPTER- 6

RESULTS AND DISSCUSSION

6.1) Compound Characteristics:

Commercial grade pesticides solution was analyzed for its various parameters under the preliminary studies before the actual treatment**.** The values of the various parameters in table 6.1.

Parameters	Value
pH of pesticides	4(Acidic)
COD	500mgL^{-1} at initial 200mgL^{-1} pesticides concentration
Max absorbance	297nm
PO_4^{-3} ions	173.2µgL^{-1}

Table 6.1: Characteristics of Commercial Monocrotophos

6.2) Absorption spectra of commercial Monocrotophos pesticides

The absorption spectrum of monocrotophos was recorded with a "UV- vis. Spectrometer (Hitachi V- 500 UV/VIS, Japan) double-beam spectrometer and scanned the sample between the range of 200 and 400nm (Figure 6.1). During the initial scanning of monocrotophos maximum absorbance came at 297nm,

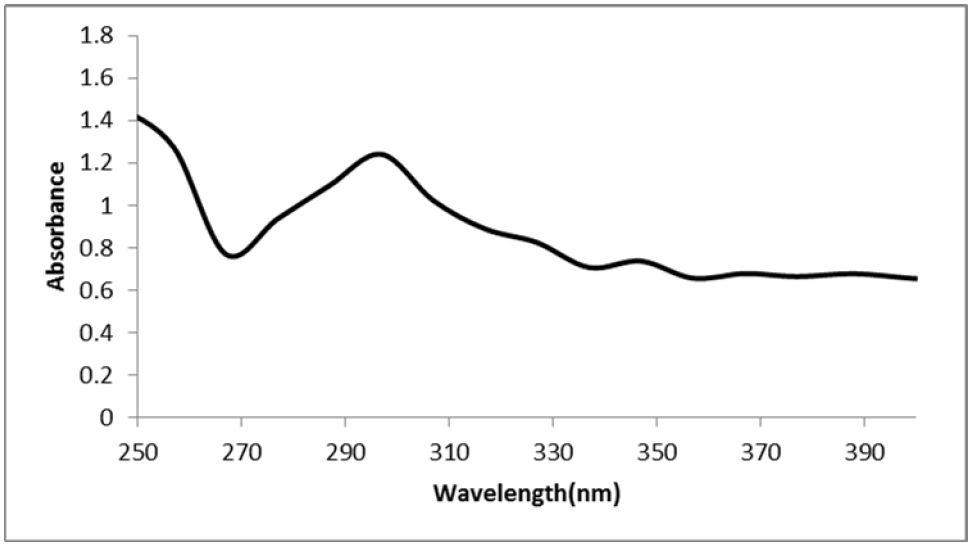

Figure 6.1: Absorption spectra of commercial grade monocrotophos pesticides

6.3) Standard curve of commercial available Monocrotophos pesticides

Standard curve for monocrotophos is prepared by plotting the graph between varying known concentration ranging from 50mgL^{-1} to 200mgL^{-1} and its absorbance at 297 (figure6.2). From this graph we can calculate unknown concentration for solution. Value of R^2 is .9876 and slope is .006

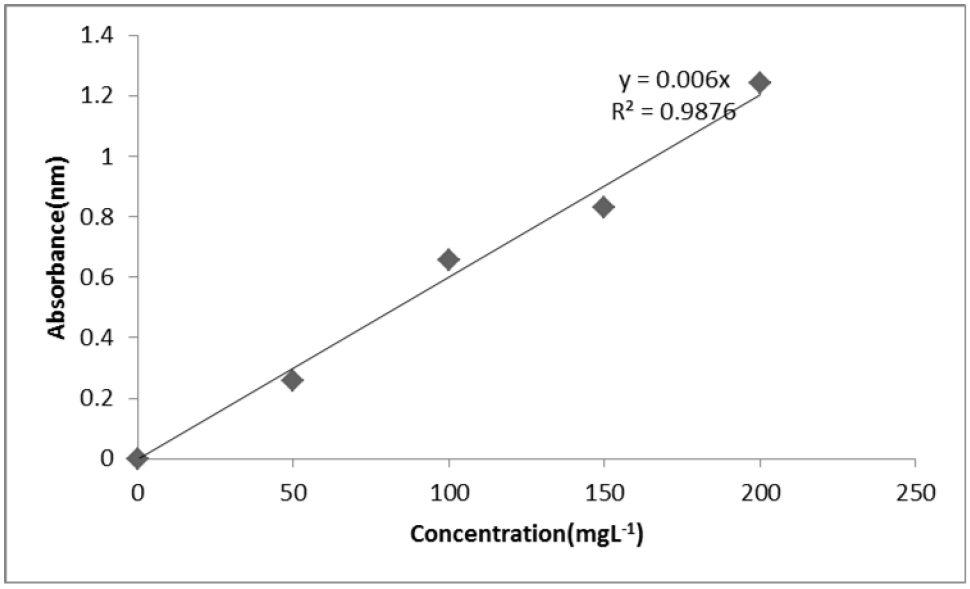

Figure 6.2: Standard curve of commercial available Monocrotophos pesticides

6.4) Preliminary Studies

6.4.1) Dark Studies (Adsorption) and Photolysis studies

To study the effect of individual parameter on the degradation, experiments were done using each parameter separately. Dark adsorption (only TiO_2) studies were carried out to know that how much adsorption was resulted either from TiO_2 or H_2O_2 instead of UV light. In the case of TiO_2 dark studies, the adsorption rate became constant after some time because of the monolayer formation on the catalyst surface. After monolayer formation, no free active sites were available for further adsorption so no further reduction in absorbance was observed. Thus results observed from adsorption experiment confirmed that decrease in concentration of compound was due to adsorption only 10% i.e. no degradation of the compound was confirmed. Only 5 to 6% degradation was observed when only H_2O_2 was added which is strong oxidant, thus confirming that degradation would be better if all the parameters used in combination mode.

In the photolysis studies, any complex compound is able to absorb of the UV light. So pesticides solution was irradiated under ultraviolet (UV) light alone in the absence of catalyst which call photolysis process. It was observed that after 3.5 hours of UV treatment the degradation was not so significant, only 35 % degradation was achieved. Thus for the complete degradation of the compound under study, some sort of advanced treatment was required

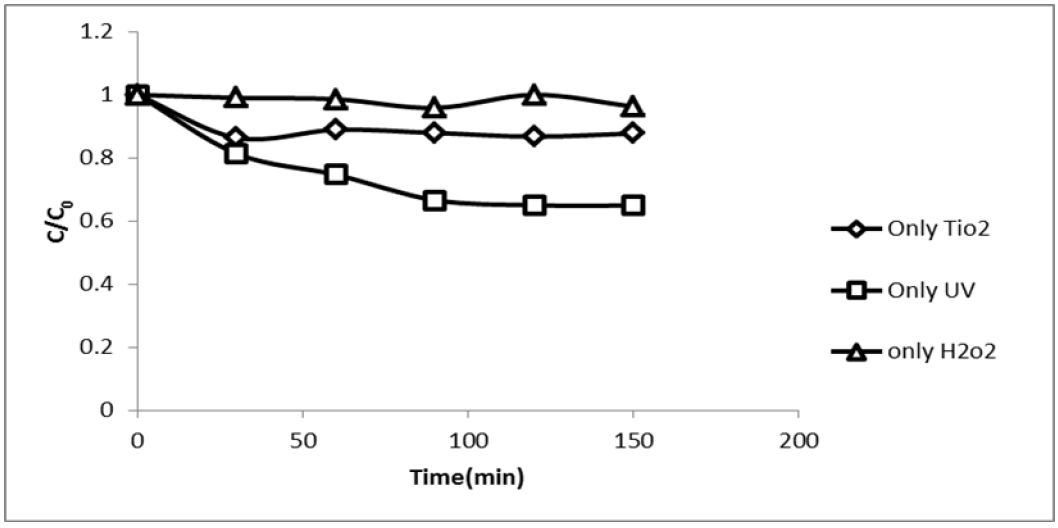

Figure 6.3: Decrease in pollutant concentration due to adsorption and photolysis phenomena

6.5) Photo catalytic Treatment and Process Optimization

After preliminary studies, the pesticide was subjected to photocatalytic treatment (UV+TiO_2) and process was optimized using the following factors:

1) Concentration of the catalyst

2) Operating pH

3) Concentration of the oxidant added

4) Initial concentration of raw compound

So the Photocatalytic treatment process was optimized for the above factors and these optimized conditions were used for the further actual treatment of the monocrotophos. Photocatalytic reactions can usually be described by a pseudo-first order kinetic expression i.e.

$-dC/dt = K C_t$. Or

i.e. $\ln C_0/C_t = kt$

Where C_0 and C_t are the concentration of monocrotophos at times 0 and t, and k is an apparent reaction rate constant.

Here plot of $\ln C_0/C_t$ V_S time (min or h) was plotted and slope of graph will be apparent reaction rate constant (min^{-1} or h^{-1}).

6.5.1) Effect of TiO_2 (Catalyst) Concentration

The effect of catalyst loading on the monocrotophos was studied in the range between 0.5 gL^{-1} to 2.5gL^{-1} at its natural pH. Plot of first order reaction rate constant (k) vs. catalyst concentration shows that it increases with the increasing catalyst concentration upto 1mgL^{-1} (Figure 6.4). After that rate constant starts to decrease. Actually at the low amount of catalyst loading, light can easily penetrate among the catalyst particle and absorb by the catalyst surface. The catalyst concentration above optimum level depends on various factors such as reactor gemotery, exposed area of catalyst, light intensity (Herrmann. J.M., 2010). So at higher concentration of catalyst loading solution become turbid and start to agglomerate which hindered the penetration of light.

At the optimum catalyst concentration 92 % degradation was achieved in 5 hours and at increasing catalyst concentration photocatalytic activity decreased due to reasons cited above.

Similar studies have been done by Nestor Javier B.P. et al., 2007 on sonophotocatalytic degradation of congo red and methyl orange in the presence of TiO_2 as a catalyst.

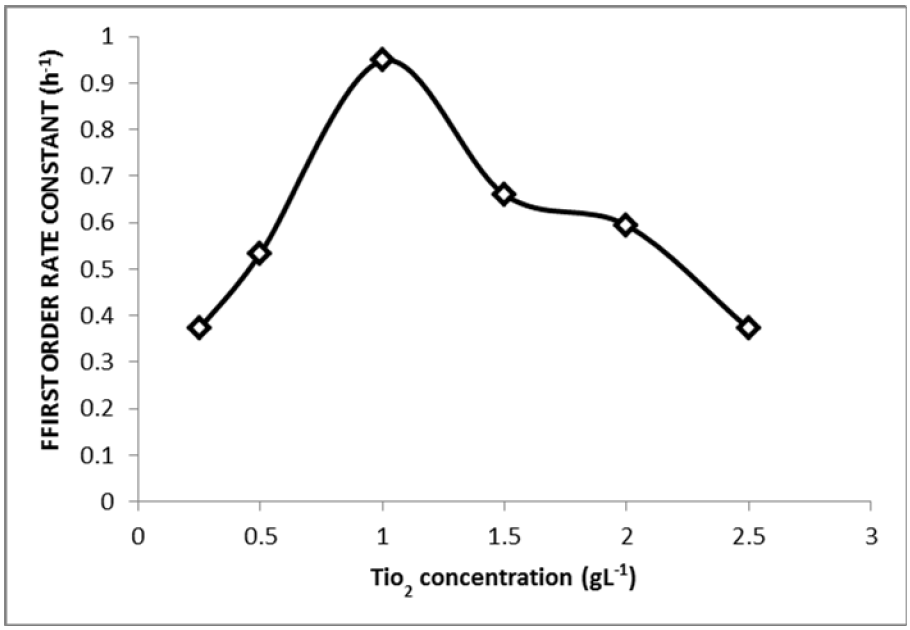

Fig 6.4: Effect of TiO_2 on rate constant {C_0 200mgL^{-1}, Natural pH 4}

6.5.2) Effect of pH

The effect of pH on monocrotophos was studied in the range of between 3 to 8 at optimum concentration of TiO_2. Initial pH was adjusted by the NaOH, H_2SO_4 (0.1N). The effect of the solution pH on the degradation rate can be explained mainly by adsorption of pollutant on TiO_2 surface. In acidic suspensions, the adsorption of pollutant on the TiO_2 particles was significantly increased comparing to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. 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..

Figure 6.5 shows that best degradation was achieved at its natural i.e. pH 4.It means monocrotophos appears with best degradation in acidic medium. At optimum pH, 92 % degradation was achieved in 5 hours. From pH 3 to pH 4, there is drastic increase in rate constant indicating formation of

intermediate anions as confirmed by the formation of large number of phosphate anions. But the rate constant decreases drastically in basic medium and remains unchanged after that.

Similar studies have been done by Demetrious et al., 2007 on the photocatalytic degradation of reactive black 5 in aqueous solutions.

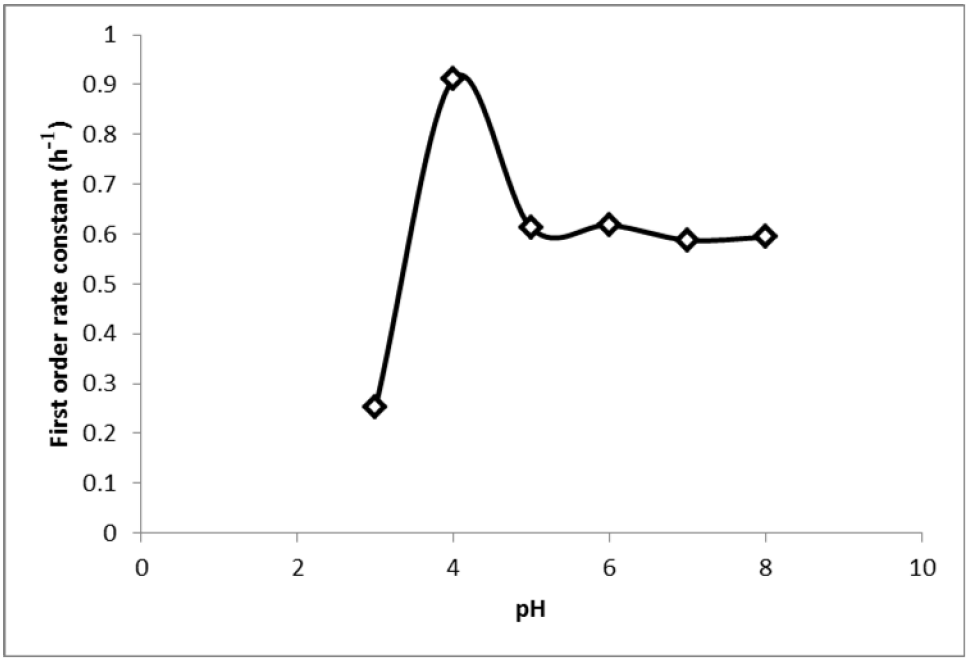

Fig 6.5: Effect of pH on rate constant {TiO_2 =1gL^{-1}, C_0 200 mgL^{-1}}

6.5.3) Effect of oxidant addition (H_2O_2)

One possible way to increase the reaction rate is to increase the concentration of OH radicals because these species are promoters of photocatalytic degradation. The addition of oxidants like H_2O_2 release OHº radicals (reaction 1) which enhance the degradation rate of monocrotophos within less period of time.

$H_2O_2 \rightarrow OH^º + OH^º$ (1)

So the effect of H_2O_2 on the degradation of monocrotophos was studied between the range of 0.375 gL^{-1} to 3 gL^{-1} at the optimum TiO_2 concentration and pH 4.

From figure 6.6, it has been observed that best results were obtained when oxidant addition was 0.375 gL^{-1} and has been taken as the optimum amount required for maximum effective treatment of

pollutant. At optimum oxidant concentration, 92 % degradation was achieved only in 2 hours at optimum catalyst and pH .

At high concentrations of H_2O_2, it also acts as a scavenger as shown in the following equations(2,3). Thus no further improvement was observed in degradation at the higher concentration of H_2O_2

$H_2O_2 + OH^\circ \rightarrow HO_2^\circ + H_2O$ (2)

$H_2O_2 + OH^- \rightarrow H_2O + O_2$ (3)

Same studies has been done by the Elmolla Emad S. et al., 2009 on the Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO_2 and $UV/H_2O_2/TiO_2$ photocatalysis

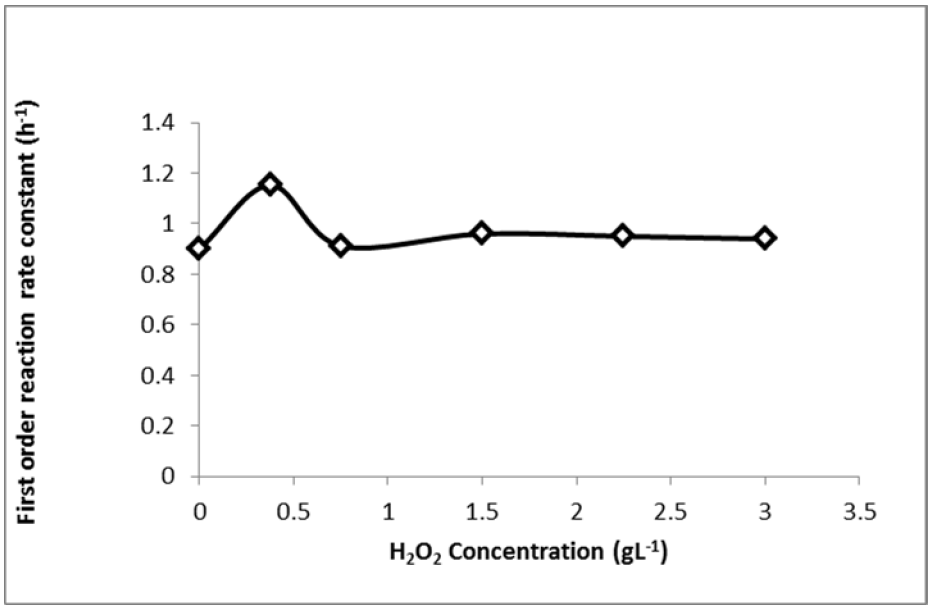

Fig 6.6: **Effect of H_2O_2 on rate constant (k) {TiO_2 =1 gL^{-1}pH 4, $C_{0=}$ 200 mgL^{-1}}**

6.5.4) Effect of Initial concentration of monocrotophos

The effect of initial monocrotophos concentration on photocatalytic degradation was studied in concentration range of 50mgL^{-1} to 200mgL^{-1}. Figure 6.7 is plotted between the initial

monocrotophos concentration and rate of reaction ($mgL^{-1}.min^{-1}$). Rate of reaction is calculated by the multiplication of rate constant and initially concentration of monocrotophos.

According to figure 6.7, it can be observed that the degradation rate increases with an increase in the monocrotophos concentration until 150 $mgL^{-1}$and then it levels off. At optimum initial concentration, 91.45 % degradation was achieved only in 3 hours. The reason for this can be explained by considering the formation of hydroxyl radicals.

Under such conditions the reaction extent between OH radicals and monocrotophos molecules increases until the monocrotophos concentration has reached 150 mgL^{-1} and on further increase in monocrotophos concentration, the rate start to drop down because the monocrotophos concentration exceeds the concentration of hydroxyl radicals produced.

Similar studies have been done by Madhavan J. et al., 2010 on Ultrasound assisted photocatalytic degradation of diclofenac in an aqueous environment

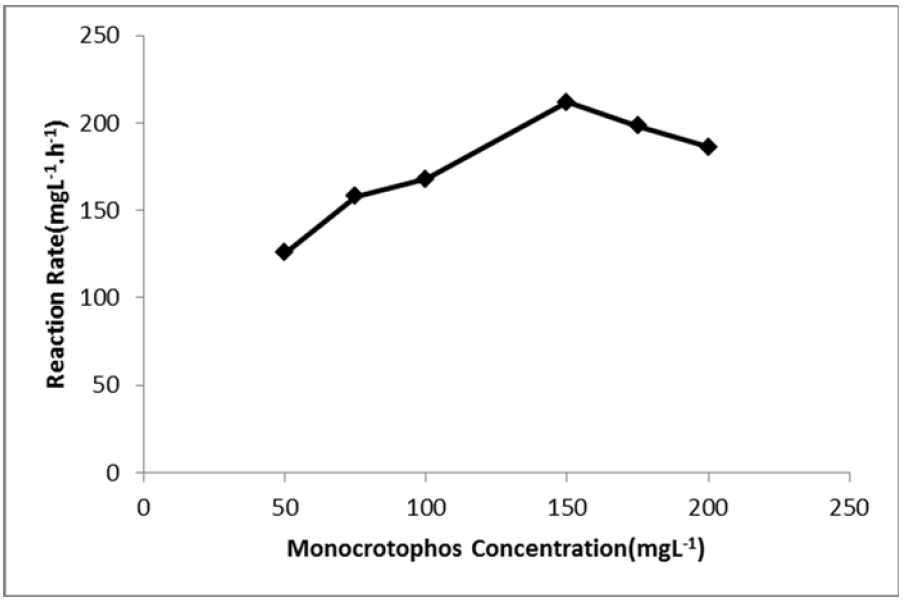

Fig 6.7: Effect of MCP initial concentration on rate constant

{ TiO_2=1gL^{-1},pH= 4,C_0=200mgL^{-1},H_2O_2=0.375gL^{-1}}

6.6) Comparitive study between artificial UV light and natural sun light for the degradation of monocrotophos

The effect of sunlight on the degradation of compound by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of compound in both

solar and UV light. In sun light treatment, the aqueous suspensions of TiO_2, containing compound solution was exposed to solar in glass bowl reactor under optimized condition of UV light treatment **{ TiO_2=1gL^{-1},pH 4, $H_2O_{2=}$ 0.375 gL^{-1} }**

According to figure 6.8, 92 % degradation of monocrotophos found in 2 hour UV light treatment under optimization condition. But under sun light treatment, 94 % degradation was found in 2 hours treatment. Results confirm the commercial applications of the technology where naturally available sunlight can be used for the degradation of the pesticides.

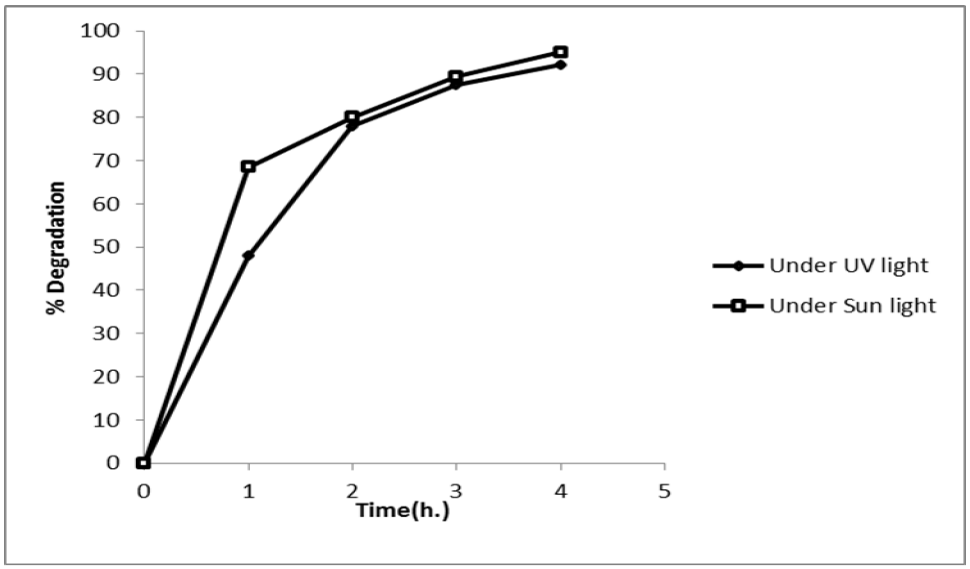

Figure 6.8: Effect of UV or Solar light on photocatalytic degradation of compound {TiO_2=1gL^{-1}L, pH 4, and $H_2O_{2=}$0.375 gL^{-1}}

6.7) Preliminary Studies of Ultrasonication treatment

6.7.1) Sonolytic (US) and Sonocatalytic treatment (US+TiO_2)

Ultrasound irradiation is new approach and emerging technology in AOP for toxic compound degradation which further enhances the water treatment by forming cavity on the surface of liquid and ultimately helps to produce OH°. Many several factor produce effect on the efficiency such as intensity of ultrasound, temperature, complexity of the substrate.

In this approach, the effect of ultrasound only (sonolysis) was studied on the degradation of pesticide monocrotophos. TiO_2 was use along with the US. Only 8 to 10% degradation was found due to sonication. Actually H_2O molecule break and released OH° radicals as per the literature but

these radicals cannot react with the compound due to absence of some source of light or proper combination.

Similar studies done by the Tangestaninejad S. et al., 2008 on sonochemical and visible light induced photochemical and sonophotochemical degradation of dyes catalyzed by recoverable vanadium-containing polyphospho molybdate immobilized on TiO_2 nanoparticles.
The use of photocatalyst and oxidant addition further raises the degradation level and it is clear from the following figures 6.9 that degradation was better achieved with US+ TiO_2+ H_2O_2 followed by US + TiO_2 and then US.

Same effect have been shown by Zhiming D. et al., 2005 on the degradation of 4-Chlorophenol.

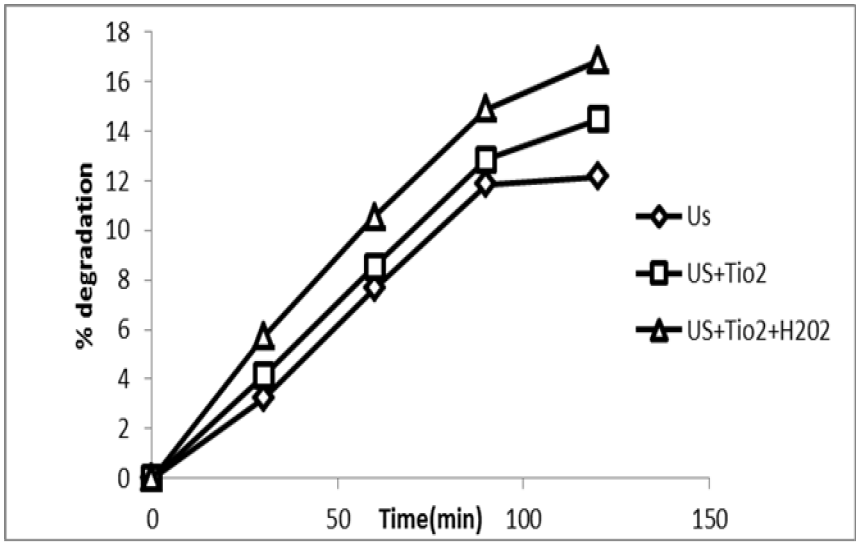

Fig 6.9: % Degradation rate due to Sonolytic (US) and Sonocatalytic (US+TiO_2) and Sonocatalytic + oxidant processes (US+TiO_2+H_2O_2) {C_0=200mgL^{-1}, TiO_2 =1gL^{-1},pH=4 H_2O_2=0.375mgL^{-1} }

6.8) Sonophotocatalytic (UV+US+TiO_2+H_2O_2) treatment

Sonophotocatalysis as an emerging treatment process improves the overall efficiency of the AOPs and chemical reaction kinetics. In the sequential experiment of photocatalysis and sonolysis, best results were achieved in the combination of these two technologies. Such combination has more additive effect which leads to enhance the degradation by generating the more and more OH°

radicals. Sonophotocatalysis degradation of monocrotophos was performed at the optimum condition of photocatalysis and 97% degradation was achieved in 2 hours which was higher than photocatalysis (Figure 6.10) because it contributes to the effectiveness of photocatalytic degradation reactions by resolving problems related to the opacity and porosity of the catalyst support as compared to individual treatments i.e. Sonolysis and Photocatalysis.

Madhvan J. et al.,2010 studied on combined advanced oxidation process for the synergistic degradation of IBP(anti-inflamentory drug)) and degradation was 85% under the sonophotocatalysis process which was 24% more compared to both individuals treatment .

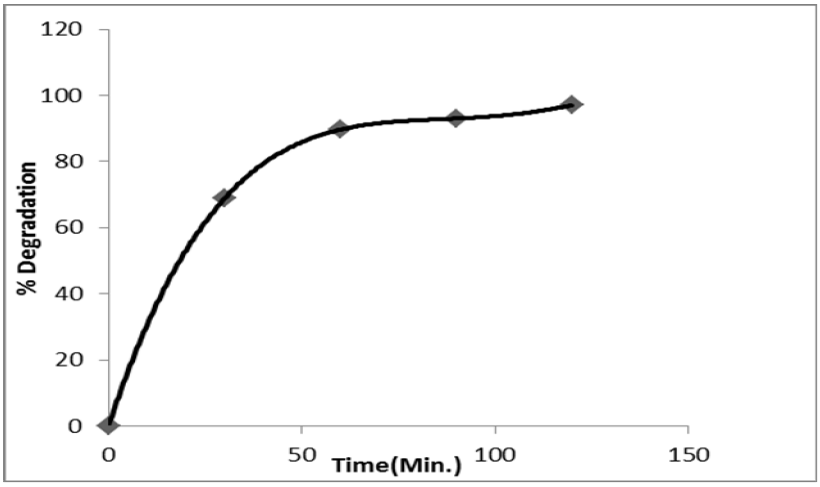

Figure 6.10: Effect of sonophotocatalytic degradation monocrotophos at the optimum condition of photocatalysis {C_0=200 mgL^{-1}, TiO_2=1gL^{-1},pH =4, $H_20_{2=}$0.375gL^{-1} }

6.9) Comparisons of Sonolysis , Photocatalytic and Sonophotocatalytic treatment.

The reason for this is that the basic mechanism for both ultrasound and photocatalytic oxidation is generation of free radicals because if these modes of irradiations are operated in combination, more no. of radicals will be available for the reaction. **Figure** 6.11 shows that by increasing the rate of reaction max degradation were achieved under Sonophotocatalytic treatment of monocrotophos i.e. 97 % after 2 hours of reaction time.

As compared to photocatalytic treatment i.e. 92% after 2 hours and very less under sonolysis process i.e. only 8 to 10 % after 2 hours. So relatively more degradation occurs in sonophotocatalytic treatment.

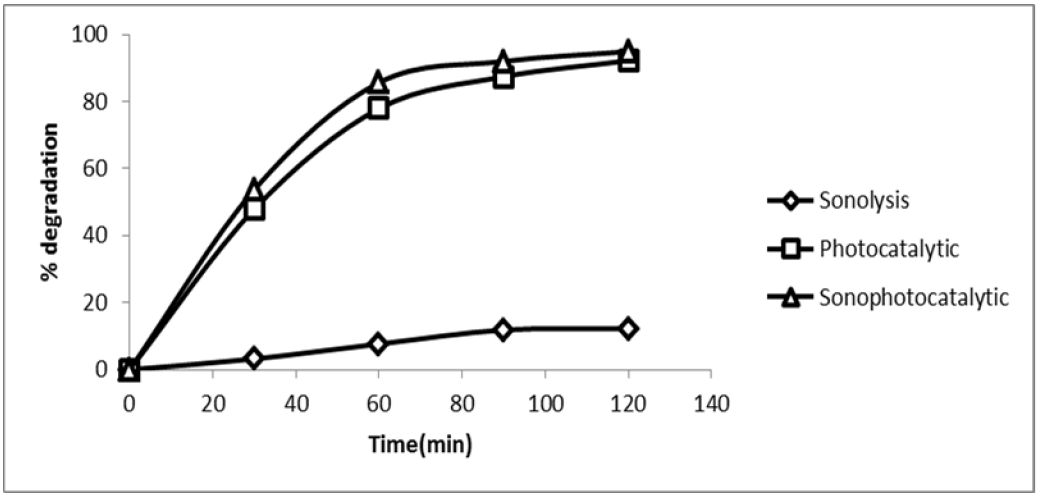

Figure 6.11: % Degradation rate due to Sonolytic (US) and Photocatalytic(UV+TiO_2) and Sonophotocatalytic(US+UV+TiO_2+H_2O_2) {C_0=200 mgL^{-1}, TiO_2 =1 gL^{-1}, pH=4, H_2O_2= 0.375 gL^{-1} }

6.10) Mineralization Studies

6.10.1) COD analysis

Main objective to the determination of mineralization of any hazardous compound with the time is to find out that in how much time any complex compound can be convert in the harmless product. The mineralization studies were done by COD analysis method. Under optimized conditions photocatalysis yielded 80% reduction in COD confirming mineralization of monocrotophos compound (C_0 200 mgL^{-1}) in 6 hours and under the sonophotocatalysis treatment 88% mineralization was achieved in 6 hour treatment(figure 6.12).

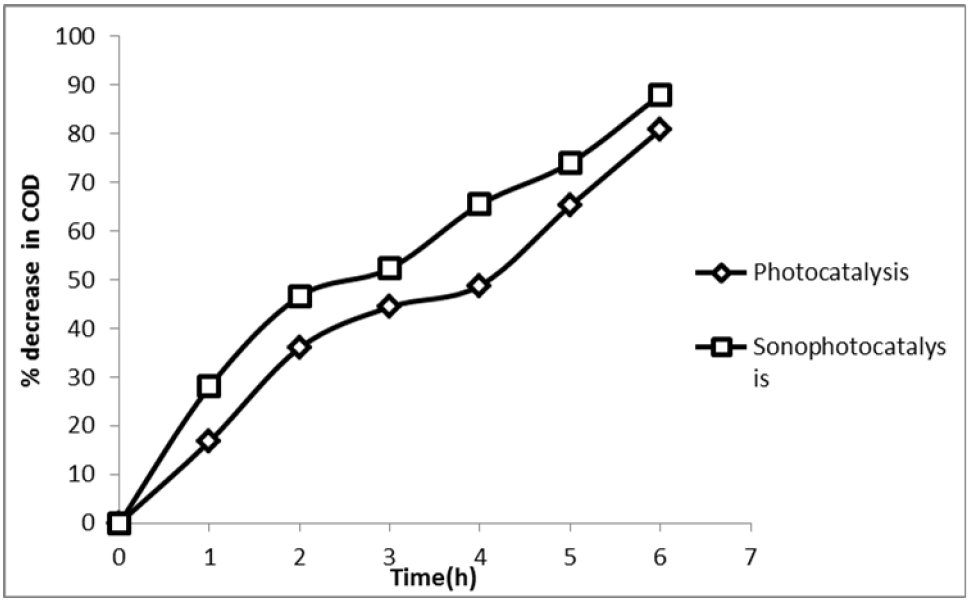

Figure 6.12: %Reduction in COD using various processes {C_0=200mgL^{-1},TiO_2=1gL^{-1} ,pH=4, H_2O_2=0.375 gL^{-1}, }

6.10.2) Measurement of Phosphate ions concentration

In the structure of monocrotophos, PO_4^{-2} group is bind one side from carbon double bond and another side from ester group by single bond. So during the degradation of monocrotophos, single bond can easily break and phosphate group are easily release. So measurement of removal PO_4^{-2} ion concentration was studied with the time at the optimum condition of catalyst, pH and oxidant under the both photocatalysis and sonophotocatalysis treatment. In figure 6.13, 92% removal of phosphate ions was found during the running of 7 hour in UV treatment after getting constant. In sonophotocatalysis treatment 98% removal of phosphate ions was found during same time confirming synergy effect of the US.

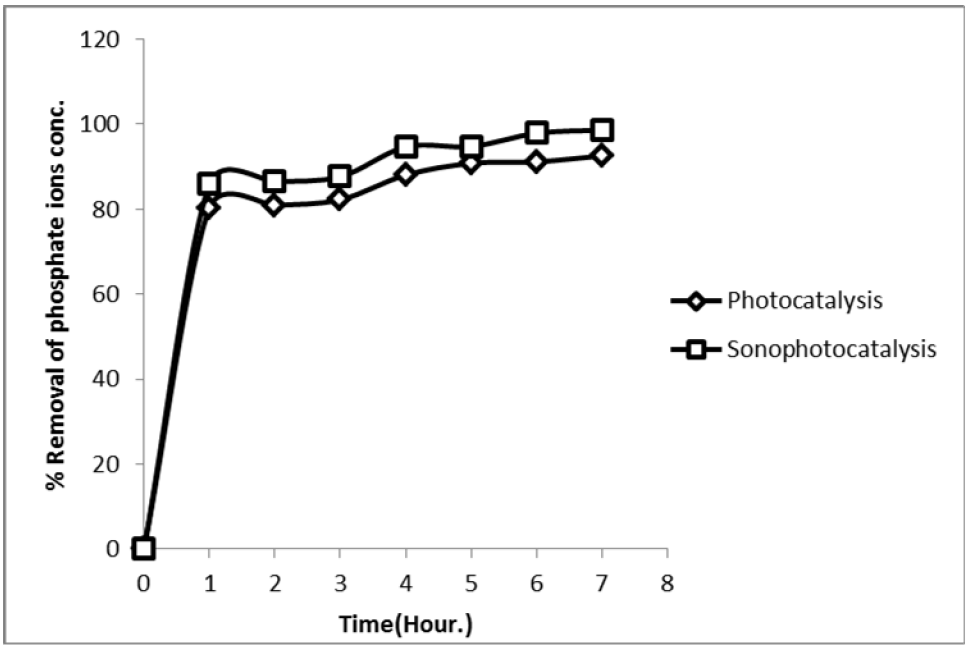

Figure 6.13: Measurment of removed phosphate ion concentration at its optimum condition {C_0=200mgL^{-1} ,TiO_2=1 gL^{-1},pH 4,H_2O_2=0.375 gL^{-1} }

6.11) Synergic effect

When the multiple process are used such as photocatalysis, sonocatalysis, sonophotocatalysis so for finding out the synergistic effect among all experiment ,synergic index is used which is based on the rate constants of all experiments. It can be quantified as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis.

$$\% \text{ Synergy} = \frac{(K_{US+UV+TiO_2+H_2O_2}) - (K_{UV+TiO_2+H_2O_2}+K_{US+TiO_2+H_2O_2})}{(K_{US+UV+TiO_2+H_2O_2})}$$

If the synergic effect is positive it means combined effect has more valuable in comparison of both individuals treatment.

In our study the rate constant of combined process $(K_{US+UV+TiO2+H2O2})$ is 1.638 hr^{-1} and rate constant of $(K_{UV+TiO2+H2O2})$ is 1.224 hr^{-1} and for $K_{US+TiO2+H2O2})$ is 0.066 hr^{-1}.

Therefore % synergy is **21.24%.**

Similar studies have been done by Elena selli, 2002, on synergic effect of sonolysis combined with photocatalysis in the degradation of an azo dye

6.12) Absorbance spectra after Sonophotocatalytic treatment

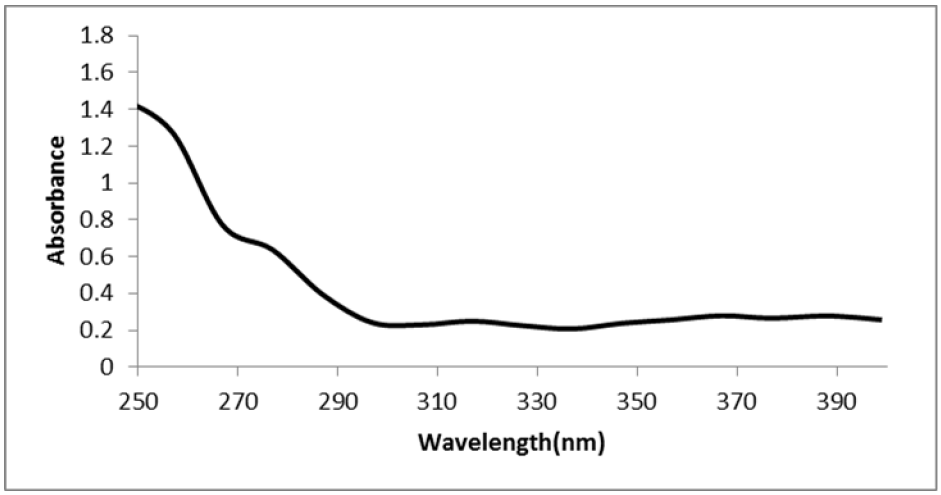

Figure 6.14 : **Absorption spectra after Sonophotocatalytic treatment**

The primary absorption peak of the raw compound commercial grade monocrotophos were at 297 nm. As the reaction proceeds, peak disappear gradually (Figure 6.14**)** and at the end of the 2 hrs of reaction time, there is no absorption peak observed. It indicates that the raw compound is degraded with the UV+US+TiO_2 system. The absence of other peaks in the degraded sample confirms that no stable intermediates are formed.

CHAPTER- 7

CONCLUSION

The quantity of pesticides compound entering the environment each year is reported to be similar to the amounts of pharmaceuticals compound used each year. Pesticides compounds are majorly suspicious environmental contaminants as they are biologically active, which obviously is a part of their nature. These intrinsic properties pose a potential for bioaccumulation and persistence in the environment.These conventional treatment technology has not sufficient potential for degradation of these such kind of complex compound. So some advance treatment technology was adopted for degradation of pesticides.

Commercial available monocrotophos pesticides has been successfully degraded in the presence of TiO_2 photocatalyst and 92 % degradation was found after only 2 hours in UV light treatment and under the optimum catalyst dose of $1gL^{-1}$, pH of 4, oxidant concentration(H_2O_2) of 0.375 $gL^{-1}$when stock solution concentration was $200mgL^{-1}$.When experiment was done in sun light under the same optimal condition than 95 % degradation was found after 2 hours. So rate of degradation was found to be slightly more in the solar light in comparison to UV light . So solar light can be efficiently method in photocatalytic degradation of pesticides Because sunlight is provided everywhere at free of cost.

Then the only Sonolysis treatment was done with all optimized conditions and the maximum degradation was achieved only 12% after 2 hours of reaction time. Sonolysis alone is not that much capable to degradation of the raw compound as it is when combined with other AOP, s like photocatalysis than rate of degradation would be more in combined treatment technology in comparison to individuals treatments.

So when sonophotocatalyst (combined treatment technology) experiment was performed under the all same optimal condition than 97% degradation was achieved only within 2 hours and 88% mineralization within 6 hours.Because sonophotocatalyst treatment enhance the treatment by releasing the more and more OH° and also enhance the mass transfer ratio.

One most important thing that synergy effect was found positive which shows that combined treatment technology has more economical and valuable effect in the degradation of monocrotophos compound.

The results of Sonophotocatalytic degradation of raw complex compound showed that it can deal with highly concentrated and toxic non-biodegradable pesticides. These technique are basically very eco-friendly and time consuming technology and most basic advantage of these technology is completely destruction of any toxic compounds into nontoxic ending products and it can be easily carried out at room temperature and atmospheric pressure. So, we can say that Sonophotocatalysis has large capability for the wastewater treatment.

CHAPTER- 8

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