TITANIUM DIOXIDE MEDIATED PHOTOCATALYTIC DEGRADATION OF CHLORPYRIFOS IN AQUEOUS PHASE

A Thesis

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CERTIFICATE

This is to certify that the report entitled ‘ **Titanium dioxide mediated Photocatalytic degradation of Chlorpyrifos in aqueous phase** ’ *submitted by* ***Ms. Poonam Yadav*** *in partial fulfilment of the requirements for the award of degree of Masters of Technology submitted in Department of Biotechnology and Environmental Sciences, Thapar University, Patiala, was carried out by her under the supervision of Er. Anoop Verma. The report has been submitted for the award of any other degree or certificate in this or any other University or Institute.*

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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ABSTRACT

Pesticides are widely utilized at various stages of cultivation and during postharvest storage to protect plants against a range of pests and /or to provide quality preservation & for the preparation of pesticide most hazardous organic and inorganic chemical are used. In developing countries, pesticides use are growing, its excessive and inadequate use leads the pollution i.e. pesticide pollution.

This organic pollutant cannot be completely degraded by conventional techniques like adsorption, coagulation and flocculation, precipitation, biological treatment etc. The incapability of conventional wastewater treatment methods to remove effectively such pollutant lead to explore new ,efficient and cost effective treatment systems. In order to meet the environment standards, the latest technologies are required to mineralize these bio recalcitrant organic compounds. Photocatalysis provides a new method for water decontamination. Recent intensive study showed that it can be applied to the degradation of many pollutants. Among them, pesticides have been considered to be one of the major pollutants to which it is promising to apply photocatalysis.

The use of high energy oxidants produces hydroxyl radical (OH) and these radicals have high oxidizing power superior to other usual oxidants and helps in complete degradation of complex organic compound into CO_2 and H_2O.This methods are called advanced oxidation processes (AOP_S), which results in formation of hydroxyl radical (OH) as a primary oxidant. The advanced oxidation process uses the H_2O_2/ UV, O_3/H_20_2, UV/O_3, and others techniques are sonolysis (ultrasonic irradiation, sonophotocatalysis etc.

In the project the technical grade pesticide Chlorpyrifos degradation was studied. Titanium Dioxide (TiO_2) is used as a Photocatalyst. The main aim of the process is to degrade the toxic complex structure of the technical grade chlorpyrifos pesticide to harmless product by treating the sample in the UV-reactor by varying pH, catalyst concentration, oxidant (H_2O_2). Degradation was followed by measuring the chemical oxygen demand (COD).

The scope of this project is to see advanced oxidation process as a viable treatment option in case of pesticides. Experiment was performed in both UV and solar light at optimized condition. The degradation of pesticide has been investigated in terms of reduction in COD. Various parameters like catalyst dose, pH, and oxidant dose these concentration and effects has been analysed. In this case catalyst concentration was optimized at 0.8 g/200 ml, pH 6.5 and oxidant concentration at 2 ml/200ml sample.

The results obtained were quit appreciable as it reduced COD from 12800 mg/L to 1800 mg/L. The results of photocatalysis got better by the introduction of high power ultrasound (i.e., sound energy with frequencies in the range of 15 kHz to ~1MHz) for the uniform distribution of the catalyst slurry. The maximum degradation of chlorpyrifos pesticide showed photocatalysis would be used as efficient and environment friendly technique for the complete degradation of toxic organic pollutants which will increase the chances of getting rid of these type of chemicals from water/wastewater. The investigations demonstrate the importance of selecting the optimal degradation parameters for practical applications of this operation.

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CHAPTER- 1

INTRODUCTION

1.0 Environmental Pollution

For normal and healthy living a conductive environment is required by all living beings, including humans, livestock, plants, microorganisms and wildlife. The favourable unpolluted environment has specific composition .When these compositions get changed by addition of harmful substances, then environment is called polluted environment. Environment pollution may be defined as any undesirable change in the physical, chemical or biological characteristics of any component of environment (air, water, soil), which cause harmful effects on various forms of life and property. Environmental pollution could be of various types: air, water, soil, thermal, noise etc.

1.1 Water Pollution

Due to its unique properties water is of multiple uses for all living organisms. Water is absolutely essential for life. Human beings depend on water for almost every developmental activity like drinking, bathing, cooking, washing, irrigation and for industrial operations. Most of water for such uses comes from natural sources from ground water, lake, rivers. Water is a universal solvent so it has property to dissolve almost all the substance in it, so it can easily get polluted. Water pollution can be caused by point and non point sources. 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, methyl mercury 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 .Some of the heavy metals like mercury, cadmium, lead, arsenic cause various type of diseases. **Fig1.1** shows how water movement takes place from atmosphere to surface.

1.2 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. A lot of water pollution is caused by factories near rivers and lakes doing illegal dumping. This hurts wildlife because the pollution will flow down the river hurting plants and animals. In some cases it can be fatal. Another big form of water pollution comes from fisherman and yacht owners. The fuel tankers from the transport lines, especially concern to marine pollution. When a fuel tanker ends up sinking it releases thousands upon thousands of gallons of fuel into the ocean. This fuel gets all over marine life and can cause serious damage to beaches and coral.

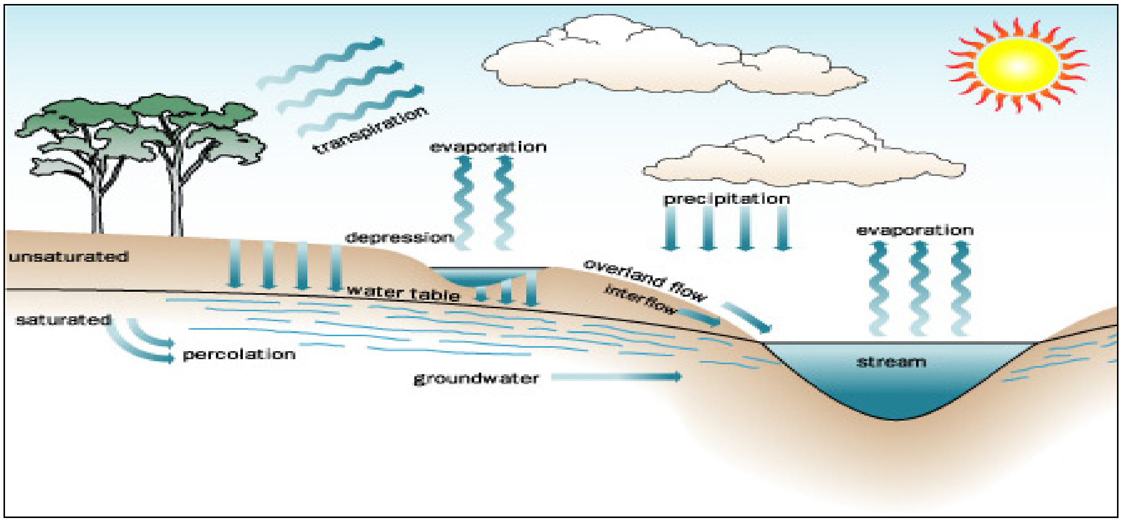

Fig.1.1 Hydrological Cycle

Another type of water pollution comes from farmers. When they spray their fields the fertilizer and insecticides can soak into the ground and get caught in a water system or river. This will then in turn hurt plant and animal life because the waterways are being poisoned. The pollution ends up hurting nature. On a more direct approach it can even pollute drinking water. Pollution caused by pesticides is also one of the biggest problem ,it pollutes the whole environment as well as cause the different types of health problems like blood cancers ,intestinal problems ,mental retardation , vomiting ,nausea ,headache , eye irritation and many more problems. These are highly toxic when it reaches into water bodies through runoff, it pollutes the aquatic bodies, because of bioaccumulation and biomagnifications property, it causes the death of aquatic organisms. **Table 1.1** shows some of the pesticides found in the drinking water, these pesticides become harmful if it exceeds certain limits .Water containing these amounts of the various pesticides shown is completely safe to drink. Furthermore, a 150-pound man would have to drink at least 75 gallons of water daily to consume even these amounts of pesticides.

Contaminant	Product type	MCL (ppm)
1,2 Dichloropropane	Fumigant	0.005
2,4-D	Herbicide	0.07
Alachlor	Herbicide	0.002
Aldicarb	Insecticide	0.003
Atrazine	Herbicide	0.003
Dibromochloropropane (DBCP)	Fumigant	0.0002
Ethylene dibromide (EDB)	Fumigant	0.00005
Glyphosate	Herbicide	0.7
Oxamyl	Insecticide	0.2
Picloram	Herbicide	0.5

T: 1.1 MCLs for several pesticides found in water (Source: USEPA 1980)

1.3 Pesticide Pollution

Pesticides are designed to control pests, but they can also be toxic (poisonous) to desirable plants and animals, including humans. These plant protecting agents called pesticides are environmentally harmful waste ***(Stievens, 1971; Hornsby et. al., 1996).***

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. 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. Pesticides being used in agricultural tracts are released into the environment and come into human contact directly or indirectly. Humans are exposed to pesticides found in environmental media (soil, water, air and food) by different routes of exposure such as inhalation, ingestion and dermal contact.

Exposure to pesticides results in acute and chronic health problems like irritation of eyes, excessive salivation to chronic diseases like cancer, reproductive and developmental disorders etc.

Different pesticides that are used in the fields of Punjab are as given below-

- Carbofuran
- Alachor
- Aldicarb
- Lindane
- Malathion
- Chlorpyrifos
- Methoxychlor

Out of all these pesticides, Chlorpyrifos insecticide from Punjab was selected for the study.

1.4 Introduction of Chlorpyrifos

The work was done on the technical grade of the Chlorpyrifos pesticide .The degradation of the technical grade Chlorpyrifos (purity 99%) was observed during the experimental work. Chlorpyrifos (trade names include Dursban and Lorsban) one of the most widely used insecticides, classified under the organophosphate pesticides.

1.4.1 Appearance: Technical chlorpyrifos is amber to white crystalline solid with a mild sulfur odour. Chlorpyrifos is registered for the control of cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, mosquitoes, and lice. It is used as an insecticide on grain, cotton, fruit, nut, and vegetable crops, as well as on lawns and ornamental plants.

1.4.2 Working of Chlorpyrifos- In animals, chlorpyrifos transforms to chlorpyrifos- Oxon, which is about 3000 times as potent against the nervous system as chlorpyrifos itself. Chlorpyrifos is linked to delayed peripheral neuropathy (degenerative lesions of sensory, motor, or reflex nerves).

1.4.3 Poisoning from Chlorpyrifos -

Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system, and the respiratory system as well as a skin and eye irritant. Acute exposure can result in such symptoms as numbness, tingling sensation, in coordination, dizziness, vomiting, sweating, nausea, stomach cramps, headache, vision disturbances, muscle twitching, drowsiness, anxiety, slurred speech, depression, confusion and in extreme cases, respiratory arrest, unconsciousness, convulsions, and death.

1.5. Objectives

- The main objectives of proposed study are :
- Survey and selection of pesticide, used mostly in Punjab region.
- Heterogeneous photo catalytic treatment of pesticide, using TiO_2 and process optimization by varying operating condition.

1.6. Approach

- By survey in Punjab region most commonly used pesticide is selected.
- The selected pesticide would be treated using AOP i.e. heterogeneous photo catalytic treatment.
- Degradation would be studied by contiously measuring the COD.
- Degradation conditions would be optimized by varying the catalyst concentration, pH and addition of suitable oxidant.
- Catalyst recycling would be checked as it could be an important step towards the economical applications.

CHAPTER–2

PESTICIDES AND THEIR CLASSIFICATION

2. A PESTICIDE AND THEIR CLASSIFICATION

2.A.0 History of Pesticides

In recent years, (basically post-World War II) chemical pesticides have become the most important consciously-applied form of pest management. Punjab has just 2.5 per cent area of the total agricultural land in India and it consumes nearly 18 per cent of the pesticides in the country. Significantly, Malwa, the cotton belt of the state, has the highest pesticide consumption density in the country. The Bhopal disaster occurred when a pesticide plant released 40 tons of methyl isocyanate (MIC) gas, a chemical intermediate in the synthesis of some carbamate pesticides. The disaster immediately killed nearly 3,000 people and ultimately caused at least 15,000 deaths.

2.A.1 Pesticide

The term "pesticide" is a composite term that includes all chemicals that are used to kill or control pests. In agriculture, this includes herbicides (weeds), insecticides (insects), fungicides (fungi), nematocides (nematodes), and rodenticides (vertebrate poisons). Now a days the agricultural production requirements cannot be satisfied without application of pesticides. Even in case of very careful treatments certain portions of the pesticides reach non-target areas, too and result in contamination of the environment. Pesticide contaminants can be expected in soil, surface water and groundwater.

2.A.1.1 Types of Pesticides

1. Bactericides

A bactericide or bactericides is a substance that kills bacteria and, preferably, nothing else. Bactericides are disinfectants, antiseptics or antibiotics.

2. 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.

3. Herbicides

An herbicide is used to kill unwanted plants. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often based on plant hormones.

4.Insecticides

An insecticide is a pesticide used against insects in all developmental forms. They include ovicides and larvicides used against the eggs and larvae of insects. Insecticides are used in agriculture, medicine, industry and the household.

5.Miticides

Miticides or acaricides are pesticides that kill mites. Different category of miticides is antibiotic miticides, carbamate miticides, formamidine miticides, mite growth regulators, and organochlorine, permethrin and organophosphate miticides.

6.Molluscicides

Mollusc ides are pesticides used to control molluscs, such as Motts, slugs and snails. These substances include metaldehyde, methiocarb and aluminium sulphate. They should be used with caution, as they can be harmful to non-target animals.

7.Nematicides

A nematocides is a type of chemical pesticide used to kill parasitic nematodes (roundworms). One common nematicide is obtained from neem cake, the residue obtained after cold pressing the fruit and kernels of the neem tree. The neem tree is by several names in the world; the tree was first cultivated in India since ancient times and is now widely distributed throughout the world.

8.Rodenticides

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. They will eat a small bit of something and wait, and if they don't get sick, they continue. An effective rodenticide must be tasteless and odorless in lethal concentrations, and have delayed effect.

9.Virucides

It is for the control of viruses.

2.A.2 Pesticide Properties

2.A.2.1 Toxicity - Mammalian and non-mammalian toxicity usually expressed as LD_{50} ("Lethal Dose": concentration of the pesticide which will kill half the test organisms over a specified test period). The lower the LD_{50}, the greater the toxicity; values of 0-10 are extremely toxic. In **Table 2.1** Characteristics of some commonly used herbicides is given with relative toxicity to fish. Toxic response (effect) can be acute (death) or chronic (an effect that does not cause death over the test period but which causes observable effects in the test organism such as cancers and tumours, reproductive failure, growth inhibition, teratogenic effects, etc.)

Herbicide	**Solubility in runoff**	**Mobility in soil water**	**Half-life in days**	**Relative toxicity to fish[1]**
MSMA	high	high	100	very low
Benefin	high	low	30	very high
Dicamba Salt	low	high	14	low
2,4-D Amine Salt	low	medium	10	very low
MCPP Amine Salt	low	high	21	low
Pendimethalin	high	low	90	high
Glyphosate Amine Salt	high	low	47	very low
Metribuzin	medium	large	40	medium

T.2.1 Characteristics of some commonly used herbicides, with relative toxicity to fish Source - (U.S. Environmental Protection Agency, 1992).

Lethal Dose (LD50)

"Lethal Dose Fifty" (LD50) is one way the toxicity of chemicals are measured. LD50 is the amount of a pesticide that has killed half of the animals in a laboratory test. The LD50 is found for both dermal and oral routes of exposure. For example, an acute oral LD50 indicates the amount of pesticide swallowed that has killed half of the animals tested.

The smaller the LD50 value, the less chemical required to kill half of the test animals and the more poisonous the pesticide. So, a pesticide with a dermal LD50 of 25 (rat) is more poisonous than a pesticide with a dermal LD50 of 2000 (rat).

Table 2.2 compares the toxicities of common products with pesticides. LD50's for different chemicals can only be compared if the same test animal was used, and even then it cannot be taken as an indication of the full toxic potential of either chemical.

Pesticide	**LD$_{50}$ (Rat) in mg/kg**	**Other product with about equal toxicity**
TCDD (Dioxin¨)	0.0002	Ricin (castor bean extract)
Saran (GB nerve gas)	0.2	Black widow spider venom
Flocoumafen (rodenticides)	0.25	Strychnine
Aldicarb (insecticide)	0.9	Nicotine alkaloid (free base)
Phorate (insecticide)	1.0	Heroin
Parathion (insecticide)	2.0	Morphine
Carbofuran (insecticide)	8	Codeine
Nicotine sulfate (insecticide)	50	Caffeine
Paraquat (herbicide)	150	Benadryl (antihistamine)
Carbaryl (insecticide)	250	Vitamin A
Acephate (insecticide)	833	Salt substitute (KCl)

T: 2.2 Comparative toxicity of pesticides and natural products, Source (1995 Farm Chemicals Handbook).

2.A.2.2 Persistence

Persistence describes the staying power of a chemical. A pesticide that is persistent will maintain its structure, or stay a long time. Pesticides are broken down (degraded) at different rates by soil microorganisms, chemical reactions, and sunlight. If the soil is moist and warm, microbes use the pesticide molecules as a food source and turn them into harmless molecules such as carbon dioxide and water. Breakdown processes occur mainly in the root zone. Breakdown is considerably slower in deeper soils and sediments. Some pesticides form intermediate substances during the breakdown process which can be more toxic than the original compound. Persistence is usually measured in terms of half-life.

2.A.2.3 Adsorption

Adsorption is the most important characteristic of a pesticide, affecting its potential to leach to ground water. Adsorption describes how tightly a compound becomes attached to soil particles. Pesticides that are strongly adsorbed (tightly held) will be less mobile in soil that is leached with water and will be less likely to reach ground water. Some pesticides may be too tightly adsorbed to give proper pest control. Injury to sensitive rotational crops may sometimes occur when a pesticide used on the previous crop is later released (desorbed) from the soil particles in amounts great enough to cause injury.

2.A.2.4 Solubility

Solubility is the tendency of a chemical to dissolve in a solvent. It is another property that affects the behaviour of a pesticide in the soil. As water percolates through soil, it carries water-soluble chemicals with it. This process is called leaching.The higher the water solubility value, the more soluble the chemical. For instance, a pesticide with a water-solubility value of 33,000 ppm at 80° Fahrenheit (27° Celsius) is much more water-soluble than a pesticide with a water- solubility value of 33 ppm at 80° Fahrenheit (27° Celsius). It is also more likely to leach. In table **T 2.3** ,list of different types of chemicals are given with their solubility property like methyl parathion that have low solubility and five days of life ,insecticides are given with different solubility property.

Chemical	**Water Solubility**	**Half-life (days)**
Methyl Parathion insecticide	low	5
Carbaryl insecticide	low	10
PCNB fungicide	very low	21
Disulfoton insecticide	low	30
Malathion insecticide	low	1
Chlorthalonil fungicide	very low	30
Phorate insecticide	low	60
Diazinon insecticide	low	40
Methamidophos insecticide	high	6

T: 2.3 Properties of some of the most commonly used pesticides in Texas (Source: USEPA-OPP. Dec., 1988)

2.A.2.5 Volatility

Volatility is the tendency for a liquid or a solid to change into a gas. Volatility describes how quickly a liquid will evaporate when it is in contact with air. Highly volatile chemicals are easily lost to the atmosphere. Some pesticides, such as fumigants, must be volatile in order to move and provide uniform distribution through the soil profile.

2.A.3. Movement of pesticides in the environment

The widespread use and disposal of pesticides by farmers, institutions and the general public provide many possible sources of pesticides in the environment. Following release into the environment, pesticides may have many different fates. **Fig: 2.1** shows pesticides which are sprayed can move through the air and may eventually end up in other parts of the environment, such as in soil or water. Pesticides which are applied directly to the soil may be washed off the soil into nearby bodies of surface water or may percolate through the soil to lower soil layers and groundwater. Pesticides which are injected into the soil may also be subject to the latter two fates.

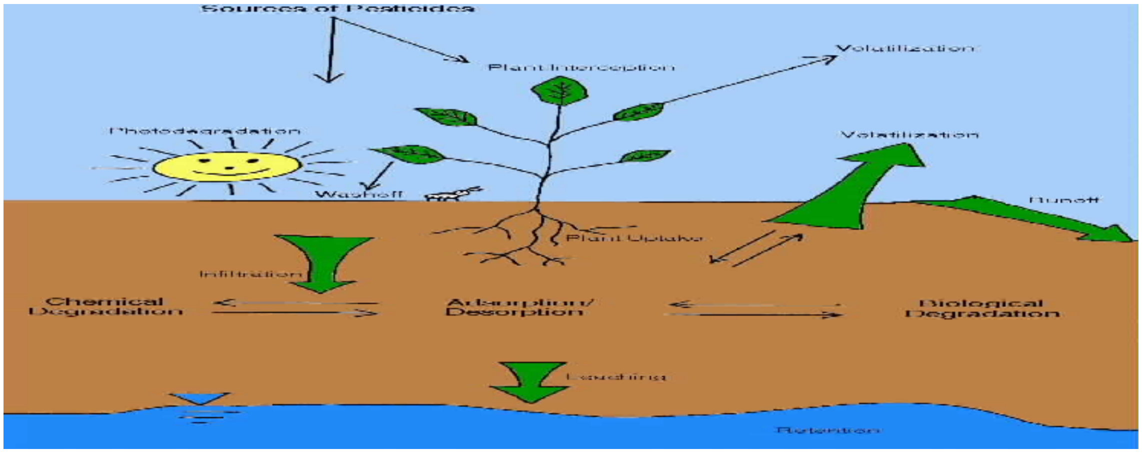

Fig : 2.1. Different modes of pesticide contamination in environment

The application of pesticides directly to bodies of water for weed control, or indirectly as a result of leaching from boat paint, runoff from soil or other routes, may lead not only to build up of pesticides in water, but also may contribute to air levels through evaporation.

This incomplete list of possibilities suggests that the movement of pesticides in the environment is very complex with transfers occurring continually among different environmental compartments. In some cases, these exchanges occur not only between areas that are close together (such as a local pond receiving some of the herbicide application on adjacent land) but also may involve transportation of pesticides over long distances. The worldwide distribution of DDT and the presence of pesticides in bodies of water such as the Great Lakes far from their primary use areas are good examples of the vast potential of such movement.

While all of the above possibilities exist, this does not mean that all pesticides travel long distances or that all compounds are threats to groundwater. Two things may happen to pesticides once they are released into the environment. They may be broken down, or degraded, by the action of sunlight, water or other chemicals, or microorganisms, such as bacteria. This degradation process usually leads to the formation of less harmful breakdown products but in some instances can produce more toxic products.

The second possibility is that the pesticide will be very resistant to degradation by any means and thus remain unchanged in the environment for long periods of time. The ones that are most rapidly broken down have the shortest time to move or to have adverse effects on people or other organisms. The ones which last the longest, the so-called persistent pesticides, can move over long distances and can build up in the environment leading to greater potential for adverse effects to occur.

Effect on environment

Pesticides, especially the organochlorine and organophosphate tend to persist in the environment, causing several types of damages including lowering of biodiversity, soil and water contamination.

Once released into the environment, pesticides tend to build up in the fatty tissues of living organisms, causing serious harm to the health of species and a potential loss of bio-diversity. Excessive use of persisting pesticides in the fields also have caused surface and underground water contamination are illustrated by records of some international studies. Methyl bromide one of the mostly used pesticides for soil fumigation in many countries have also been identified as the major contributor of ozone depletion ***(Giri 1998).***

2.A.4. Movement of pesticides in soil

Persistence is measured as the time it takes for half of the initial amount of a pesticide to breakdown. Thus, if a pesticide's half-life is 30 days, half will be left after 30 days, one-quarter after 60 days, one-eighth after 90 days and so on. It might seem that a short half-life would mean a pesticide would not have a chance to move far in the environment. This is generally true; however, if it is also very soluble in water and the conditions are right, it can move rapidly through certain soils. As it moves away from the surface, it moves away from the agents who are degrading it such as sunlight and bacteria. As it gets deeper into the soil, it degrades more slowly and thus has a chance to get into groundwater.

The downward movement of non-persistent pesticides is not an unlikely scenario and several pesticides with short half-lives, such as aldicarb, have been widely found in groundwater. In contrast, very persistent pesticides may have other properties which limit their potential for movement throughout the environment. Many of the chlorinated hydrocarbon pesticides are very persistent and slow to breakdown but also very water insoluble and tend not to move down through the soil into groundwater. They can, however, become problems in other ways since they remain on the surface for a long time where they may be subject to runoff and possible evaporation. Even if they are not very volatile, the tremendously long time that they persist can lead, over time, to measurable concentrations moving through the atmosphere and accumulating in remote areas.

2.A.5. Pesticide movement in water

There are two routes of movement of pesticides into water sources as shown in **fig.2.2.**

- **Runoff** - physical transport of pesticides over the ground surface by rainwater which does not penetrate the soil or carried with transported sediment.
- **Leaching** – movement of pesticides downward through the soil by rain or irrigation water.

When pesticides are applied on fields, gardens, parks, and other places, a percentage of the chemicals end up as runoff. This runoff moves in streams, rivers, and lakes. Similarly, when pesticides are applied on lawns in urban and suburban areas, rain washes some of the into pesticides streets gutters, where the pesticide-contaminated water goes through storm and drains and pipes and eventually flows into nearby creeks, and rivers.

Some of the pesticides also end up in groundwater systems by leaching down through the soil. Small amounts also volatize into the atmosphere, and then later fall back to land as precipitation. As a result of all these pathways, pesticides are widely found in rivers, streams, lakes, and even in drinking water.

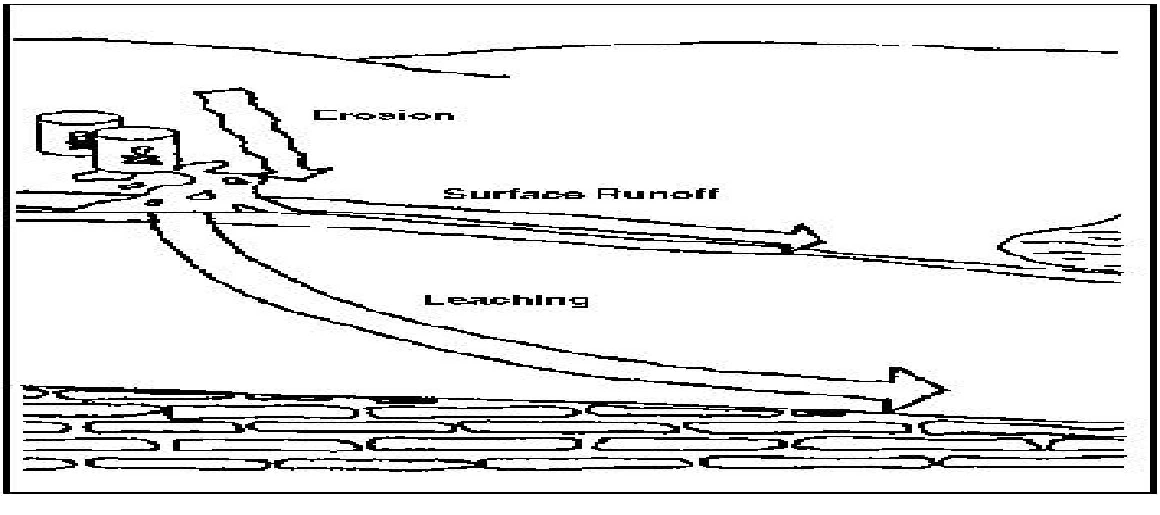

Fig : 2.2. Pesticides can pollute water through either surface runoff or leaching

The over-application or misuse of pesticides and other agricultural chemicals (such as fertilizers) can allow these chemicals to enter surface and ground water. Drift, evaporation and wind erosion can carry pesticide residues into the atmosphere. From there they can fall in rain or snow to contaminate lakes and streams. Using excessive amounts of chemicals on open or porous soils where there are shallow water tables can allow pesticides to leach or percolate into the ground water.

Improperly cleaning or disposing of containers, as well as mixing and loading pesticides in areas where residues or run-off are likely to threaten surface or ground water, are other potential sources of contamination. Some pesticide labels and some state statutes specify safe distances from well heads for pesticide mixing and loading.

2.A.6. Pesticide pollution

2.A.6.1 Pesticide pollution –Pesticides are poisons designed to destroy unwanted life forms. (Environmental Protection Agency, 1990) estimates about more than 600 million pounds of pesticides enter the environment each year in the United States. The EPA estimates its potential to pollute water. Pesticide manufacturers and the EPA use this information to develop specific precautions to prevent pesticides from entering water. These precautions are printed on the product's label

2.A.6.2 Ecological effects of pesticides

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, although terrestrial impacts by pesticides do occur, the principal pathway that causes ecological impacts is that of water contaminated by pesticide runoff. The two principal mechanisms are bio concentration and biomagnifications.

Bioconcentration: This is the movement of a chemical from the surrounding medium into an organism. The primary "sink" for some pesticides is fatty tissue ("lipids"). Some pesticides, such as DDT, are "lipophilic", meaning that they are soluble in, and accumulate in, fatty tissue such as edible fish tissue and human fatty tissue. Other pesticides such as glyphosate are metabolized and excreted.

Biomagnifications: This term describes the increasing concentration of a chemical as food energy is transformed within the food chain. As smaller organisms are eaten by larger organisms, the concentration of pesticides and other chemicals are increasingly magnified in tissue and other organs. Very high concentrations can be observed in top predators, including man.

2. B. CONSUMPTION & POISIONING OF PESTICIDES IN INDIA

2. B.1 Consumption of pesticides in India:

India ranks10th in the world in pesticide consumption as its total consumption amounts to about 500 million tonnes ***(Hundal et. al, 2006).*** Other major input for Indian agriculture is use of various pesticides, like insecticides, weedicides, fungicides, rodenticides etc. As the cropping pattern is becoming more intensive use of these pesticides is also increasing. Consumption of insecticide in agriculture has been increased more than 100% from 1971 to 1994-95. For instance, insecticide consumption in India, which was to the tune of 22013 tonnes has increased to 51755 tonnes by 1994-95. It is given in **Fig: 2.3** that consumption of all of these pesticides in same duration has increased more than two times, that is from 24305 tonnes to 61357 tonnes.

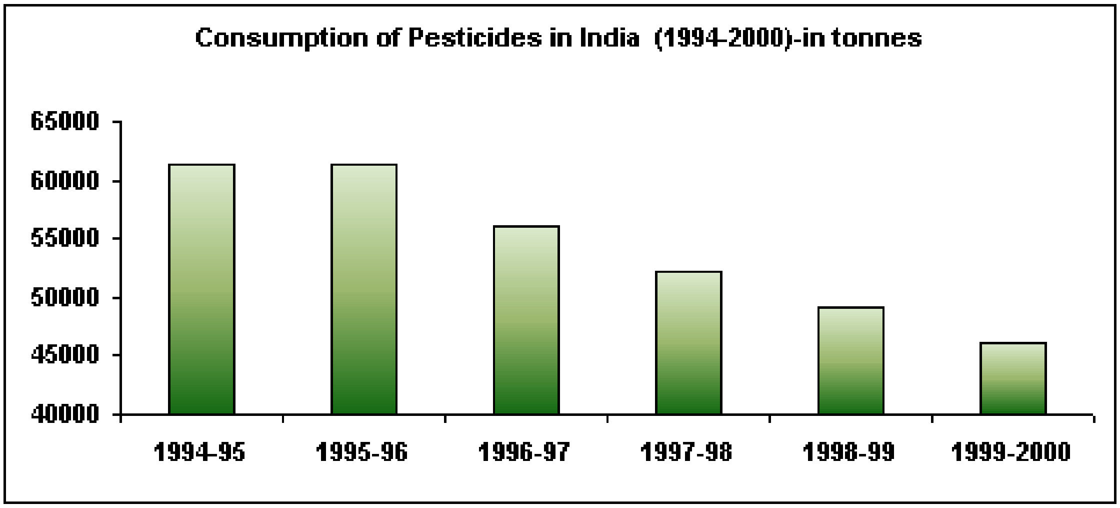

Fig: 2.3Consumption of Pesticides in India (Source: Indian Chemical Statistics 2000-01)

But in recent past, change has been observed in trends of pesticides consumption. As a consequence of adoption of bio intensive Integrated Pest Management Programme in various crops the consumption of chemical pesticide (Tech. Grade) has come down from 66.36 thousand MT during 1994-95 to 43.59 thousand MT during 2001-02 with a reduction of 27.69% (Thirty Seventh Report of Standing Committee on Petroleum and Chemicals, 2002). Consumption pattern of pesticides in India is also very different from world.

In India insecticide account for 76% of the total domestic market while herbicides & fungicides have a significantly higher share in the global market.

There are wide ranges of regional variations in pesticide consumption in the country. In the year 2000-01,

- States of Haryana, Punjab and Uttar Pradesh by consuming more than 5,000 MT (technical grade) pesticides annually come under category I
- States of, Andhra Pradesh, Gujarat, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Rajasthan, Orissa and Tamil Nadu, which consumed between 1000 MT and 5000 MT fall in the category II states.
- States viz., Assam Bihar and Himachal Pradesh that consumed pesticide between 100 and 1000 MT come under category III.
- States viz., Arunachal Pradesh, Jammu & Kashmir, Manipur, Mizoram, Nagaland, Tripura, Delhi and Union Territory (UT) of Pondicherry consumed pesticides between 10 and 100 MT annually fall under category IV.
- States viz., Goa, Meghalya, Sikkim and UTs viz., Andaman & Nicobar Islands, Chandigarh, Dadara & Nagar Haveli, Daman & Diu and Lakshadweep consumed less than 10 MT pesticides annually as fall in the last category in pesticide consumption (Thirty Seventh Report of Standing Committee on Petroleum and Chemicals, 2002).

One of the consequences of indiscriminate use of pesticide is the adverse health impact on society in general and vulnerable population like children in particular. Some of the well-known health effects of pesticide exposure include acute poisoning, cancer, neurological effects and reproductive and developmental harm. The major causes of concern in this respect are bio -accumulation of pesticides and the prolonged time period that it takes to express the negative health consequences due to the health concern some of the pesticides are banned by government as given in table **T.2.4.**

S.No.	Name of Pesticides
1	Aluminium Phosphate
2	DDT
3	Lindane
4	Methyl Bromide
5	Methyl Parathion
6	Sodium Cyanide
7	Methoxy Ethyl Mercuric Chloride (MEMC)
8	Monocrotophos
9	Endosulfan
10	Fenitrothion
11	Diazinon
12	Fenthion

T: 2.4 Pesticides banned in Indian agriculture (Source: PPCB) congenital abnormalities

T:2.5 Showing the congenital abnormalities i.e. Significantly higher in the exposed group of females as compared to the control group. Congenital heart and skeletal abnormalities were also high. Exposure linked to genotoxic agent, which could be endosulfan in this case.

	Control (% of people affected in the group)	Exposed (% of people affected in the group)
Congenital abnormalities	1.09	5.8

T:2.5 Congenital abnormalities in different groups . (Source: National Institute of Technology Calicut 2006)

Neurological problems:

T:2.6 Showing the neurological problems i.e. significantly higher prevalence of learning disabilities, low IQ and scholastic backwardness were found.Exposure to some neurotoxin agent, possibly endosulfan, during development stages.

	Control (% of people affected in the group)	**Exposed (% of people affected in the group)**
Learning disability	2.60	10.7
Retained in same class	13.50	20.40

T: 2.6 Neurological problems (Endosulfane pesticide) Source: National Institute Calicut 2006

2.B.2: Pesticide poisoning in India

Fig 2.4 showing the reported cases of pesticide poisoning in India ,during 1997 to 2002, 8040 patients were admitted to the hospital Mahatma Gandhi Memorial (MGM) Hospital, a district level government hospital in the city and district of Warangal of Andhra Pradesh ,with pesticide poisoning and 1819 of these died. The most patients in one year were 1643 in 2001 with 326 deaths (CFR 20%), the lowest 1035 in 2002 with 230 deaths (CFR 22%). The highest CFR occurred in 1999 with 24% of patients dying ***(Eddleston et. al, 2005)***

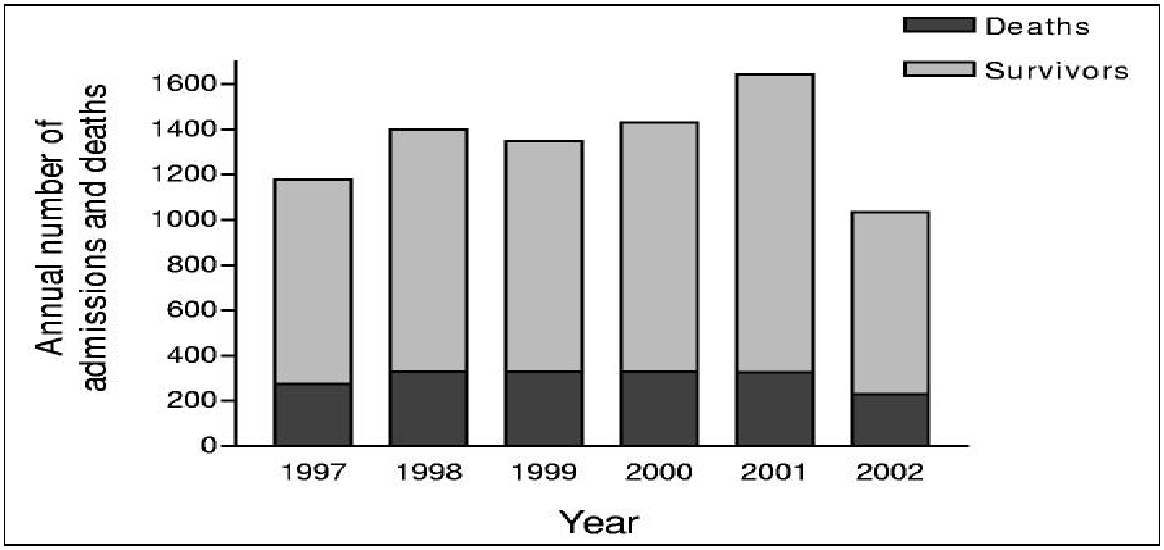

Fig:2.4 Annual number of pesticides admission and deaths at Mahatama Gandhi Memorial Hospital (1997-2002) Source: Indian Chemical Statistics 2000-01.

CHAPTER- 3

PESTICIDE CONTAMINATION IN PUNJAB

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3. A : PESTICIDE CONTAMINATION IN PUNJAB

3. A.1: Pesticide Contamination in Punjab:

Punjab has made a commercial progress after green revolution. The food grain production has increased from 3.16 million tons in 1960-61 to 24.89 million tons in 2000-2001 (source Deptt.of agricultural, govt of India).Whereas ,the initial increase in production was mainly due to increase in area under cultivation ,a secular rise of 17.9 million tons in food grain production from 1971 to 2001 can be largely attributed to intensive use of inputs like fertilizers ,pesticides ,insecticides ,herbicides and mechanization of farming. The grains resulting from the use of chemicals inputs because their ability to kill potential diseases causing organisms and control insects, weeds, and other pests , however ,have not been without their consequent environment costs. The excessive and non judicious use of these chemicals especially chemical pesticides leads to the environment degradation through air, water and soil pollution and also affects the microbial fauna present in soil.

Since pesticides, insecticides and herbicides are designed to kill or adversely affect the living organisms, by their very nature, they pose risk to humans and non target plants and animals as well. They not only contaminate the ecosystem but also bioaccumulation in the food chain and can be traced in plants and animal tissues causing serious health hazards. As per WHO estimates, pesticides lead to one million pesticide poisoning cases and 20,000 deaths every year globally.

3.A.2: Definition of Pesticide -A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pest can be insect's mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. There are mainly two types of pesticides available chemical pesticide and bio pesticides, mostly farmers use chemical pesticides.

Pesticide consumption in India has increased from 2353MT in the 1955 to 48350 MT in 2003 for technical grade chemical pesticides. At present (March 2005) 186 technical grade pesticides are registered in India for use. India pesticide industry has achieved the status of second largest basic pesticide manufacturer in Asia after Japan. Yet, the contamination of food products in the country is alarming. Above 20% of Indian food products contain pesticides residues above the tolerance level compared to only 2% globally ***(TERI, 2000).*** Pesticides usage for cultivation of food crops amongst the different states of India indicates a mixed pattern. The per hectares pesticide use is highest in Punjab (923 g/ ha) as compared to other agriculturally advanced states like Haryana (843g/ha) ,Andhra Pradesh (548g/ha),Tamil Nadu (410g/ha),Karnataka (216g/ha) and Gujarat (47g/ha) etc ***(Agnihotri,2000).***

3.A.3: Punjab State-Scenario - The state of Punjab has only 1.5% landmass of the country.However.it consumes about 15% of pesticides used in India. It is given in **Fig: 3.1,** the consumption has increased from 3300 MT in 1975 to 7200 MT in 2003 for technical grade chemical pesticides

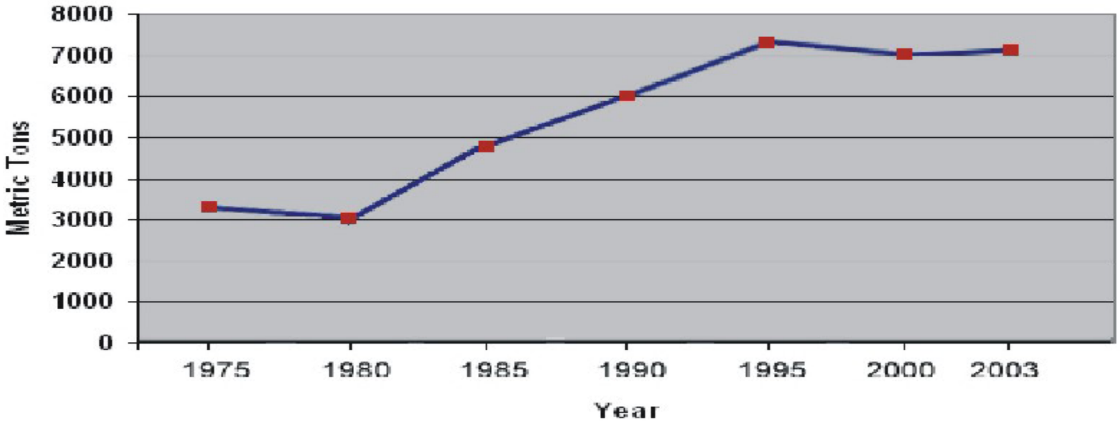


Fig:3.1 Consumption trends of pesticide in India (Source : Directorate of plant and Quaratine ,Govt of India).

Insecticides alone constitute 60 % of total pesticide of total pesticide and more than 90% of pesticide are being used in the cultivation of cotton, rice and vegetables ***(Singh 2002).***The Malwa region (cotton belt) accounts for nearly 75% pesticide used in state.

Although pesticides have played a significant role in agricultural development in the state and played a key role in making Punjab the food bowl of the country,but the ubqitous presence of pesticide residues in biotic and abiotic environment is a matter of serious concern.As per ICAR pesticide residue means any substance in food for humans or animals resulting from the use of pesticide.It includes any specified derivatives such as degration and conversion products, metabolites and reaction products which are considered to be the toxicological significance.

3.A.4: Studies conducted on pesticide residues –By the large survey ,research conducted on pesticides residues in the environment and food products. Results indicates residues of chemical pesticides in human beings ,milk,water,vegetables and other food products at levels,which are dangerous for human health.The results of these studies are briefly given below.

Residues of DDT and HCH/ BHC in wheat floor in Punjab was conducted by ***Joia et al.***,during 1974 -1976 a total 140 samples of wheat flour from flour mills and retail shops were collected from jalandhar ,patialsa,sangrur ,ludhiana,faridkot,amritsar chandhigargh (20 each from each city).residues of DDT and HCH were detected in 124 and 116 samples respectively out of 140 samples.Twenty seven samples showed DDT level more than 1 ug/gm .However in most of the samples DDT residues were reported,.The maximum level of DDT residue of 10 ug/gm were detected in one sample from Jalandhar.However residues of BHC/HCH and were found to be higher than DDT. The higher level of HCH/BHC residue of 12 ppm were found in samples of Chandigarh(WHO permissible limits of HCH/BHC in cereals is 0.1 ug/gm).The study suggested the possibility DDT contamination of wheat through sources other than direct admixture with grain.For sourceds of HCH/BHC residues, the result suggested that thepractice of mixing of HCH with wheat grain during the storage could be the main reasons,but other sources of contamination were not ruled out.

According to other studies about 54% of the total pesticides used in Indian agriculture are consumed on cotton alone, though it accounts for only 5% of the total cultivated area ***(Purl et. al, 1999)*****,** residues of DDT and benzene hexachloride were found in breast milk samples collected from mothers in Punjab. The amount of residues were very high and babies were ingesting 21times the amount of these chemicals***(Karla et. al,1994),.***and also in bovine milk (***Kalra et. al, 1999)*** fruits and vegetables from Punjab and a few reports of high incidence of cancer have been coming from certain areas of Punjab since last few years. An epidemiological study was conducted in villages of Talwandi Sabo block, district Bhatinda by the Chandigarh based Post Graduate Institute of Medical Education and Research (PGIMER) on behalf of the Punjab Government to assess whether cancer cases are higher in these areas. In another case study, Punjab is concerned; the consumption of insecticides/ pesticides is 7400 metric tones in 2001 as shown in **Fig: 3.2.** It stands 3rd with 11.80% after

Andhra Pradesh (17.90%) and Utter Pradesh (13.20%) in the total consumption of pesticides in India. In Punjab, insecticides alone constituted 60 per cent of total consumption pesticides/insecticides and more than 90 per cent of the pesticides/insecticides were used in the cultivation of cotton, rice and vegetables.

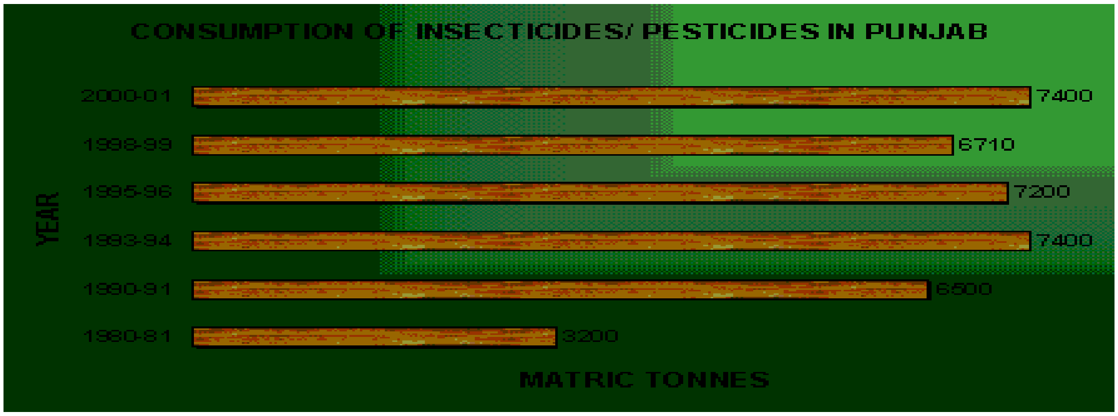


Fig:3.2 The above consumption of insecticides/pesticides includes Weedicides, Fungicides, Rodenticide (poisons).Source: Department of Agriculture, Punjab 2001

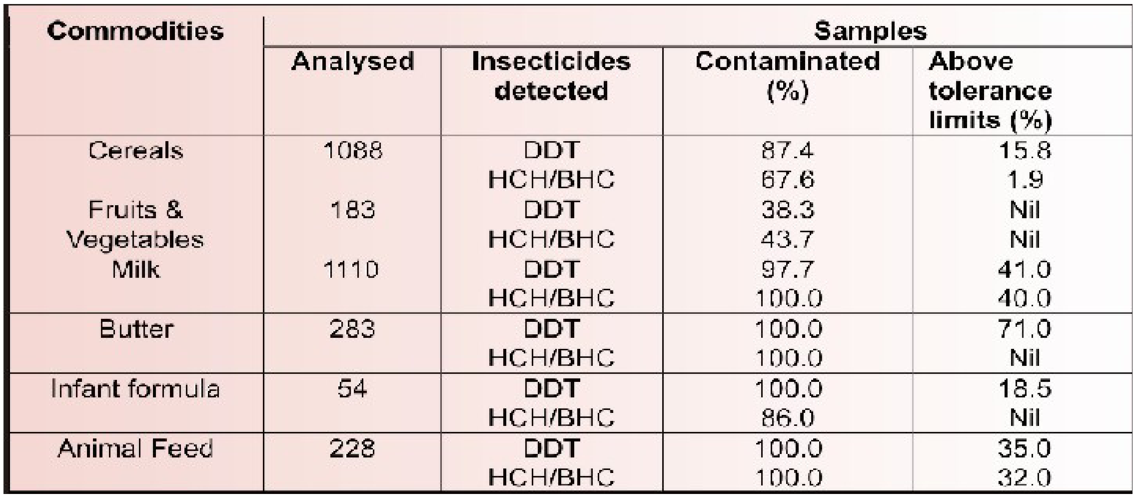
Pesticides consumption in Punjab 1975 -2005 (Metric Tonnes)

In other survey, it is found that pesticides consumption in Punjab from 1975 to 2005 it was 3300 metric tonnes in 1975 and hence it increases 6900 metrics tones in 2005 as shown in **T.3.1.**

Year	Consumption(metric tonnes)
1975	3300
1980	3000
1985	4800
1990	6000
1995	7300
2000	7005
2005(P)	6900

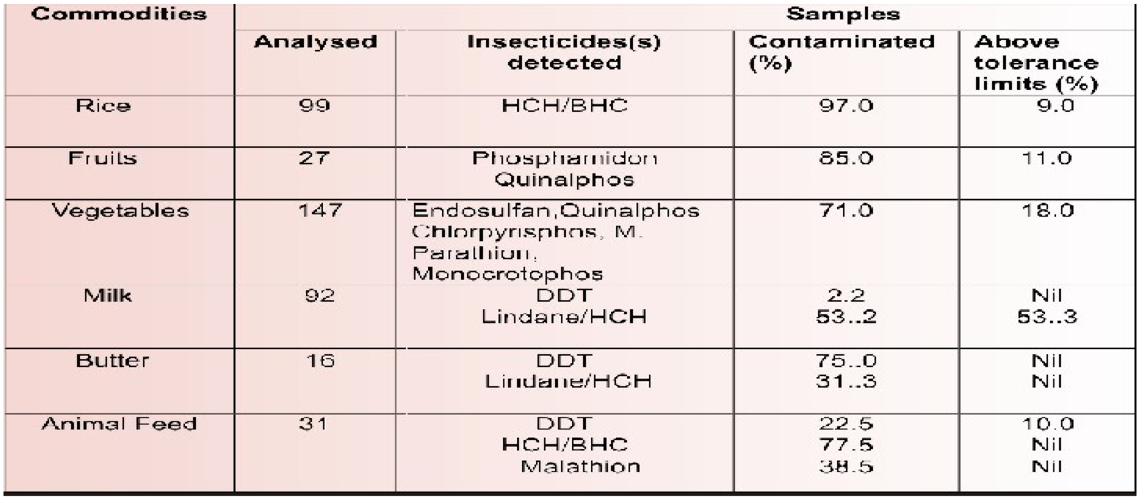
T.3.1 Consumption of pesticides in Punjab (Source: Directorate of Plant Protection and Quarantine, GoI & Central Insecticide Board and registration committee)

In year 2002, ***Balvindar Singh*** of Punjab Agricultural University in his study pesticides contamination of the environment in Punjab compared pesticide residues in Punjab during 1976-1996 with 1996-2001.The results are summarized in table **T.3.2** and **T.3.3**



Commodities	Samples			
	Analysed	Insecticides detected	Contaminated (%)	Above tolerance limits (%)
Cereals	1088	DDT	87.4	15.8
		HCH/BHC	67.6	1.9
Fruits & Vegetables	183	DDT	38.3	Nil
		HCH/BHC	43.7	Nil
Milk	1110	DDT	97.7	41.0
		HCH/BHC	100.0	40.0
Butter	283	DDT	100.0	71.0
		HCH/BHC	100.0	Nil
Infant formula	54	DDT	100.0	18.5
		HCH/BHC	86.0	Nil
Animal Feed	228	DDT	100.0	35.0
		HCH/BHC	100.0	32.0

T.3.2: Insecticides residues in different food and feed commodities in Punjab during 1976-1996 Source: Department of Entomology, PAU, 2002.



Commodities	Samples			
	Analysed	Insecticides(s) detected	Contaminated (%)	Above tolerance limits (%)
Rice	99	HCH/BHC	97.0	9.0
Fruits	27	Phosphamidon Quinalphos	85.0	11.0
Vegetables	147	Endosulfan,Quinalphos Chlorpyrisphos, M. Parathion, Monocrotophos	71.0	18.0
Milk	92	DDT	2.2	Nil
		Lindane/HCH	53..2	53..3
Butter	16	DDT	75..0	Nil
		Lindane/HCH	31..3	Nil
Animal Feed	31	DDT	22.5	10.0
		HCH/BHC	77.5	Nil
		Malathion	38.5	Nil

T.3.3: Insecticides residues in different food and feed commodities in Punjab during 1996 -2001 Source: Department of Entomology, PAU, 2002.

Data indicates that,between1976 to 1996 the major pesticides used in agriculture were DDT and BHC/HCH, the trend shifted to other organic pesticides thereafter, especially due to ban on use of DDT in agricultural as given in **T.3.3**. However, HCH/BHC was still used on cereals (97% rice sample indicating contamination). Further, the % contamination samples of fruits and vegetables with other persistent organic chemicals have also increased during 1996-2001, indicating their higher use in perishable, ready to market food products. The % sample of these product with residues of pesticides above tolerance limits has also increased, which is a case of concern. However, the contamination of milk and butter with DDT has distinctly reduced.

The Punjab Pollution control Board has also initiated studies on Estimation of Pesticides in River Water Since 2002 ***(Tiwana et.al, 2005)*** .The data for river Sutlej, Beas and Ghagger in water and sediments is presented in **Fig:3.3** to **Fig:3.8**.

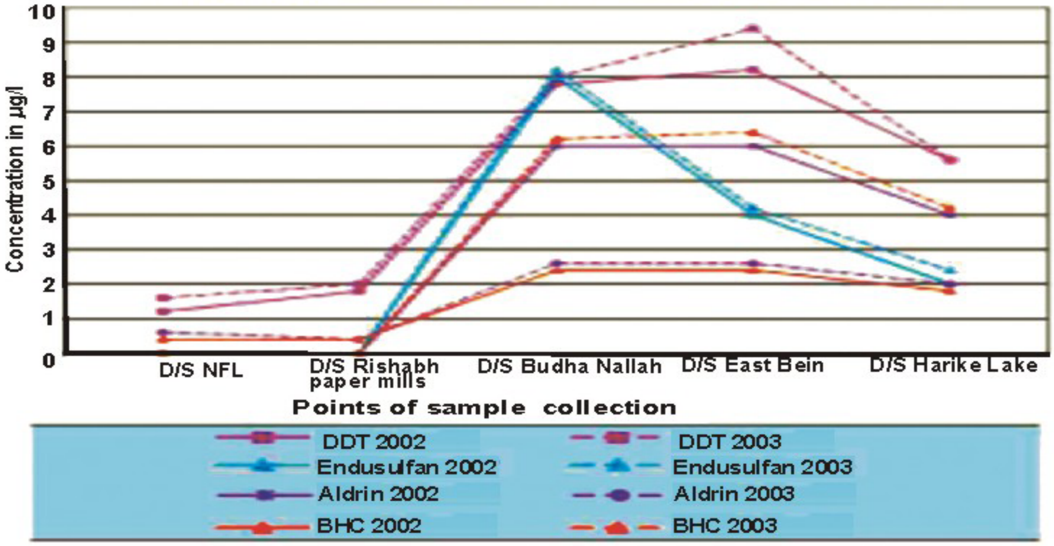


Fig:3.3 Concentration of pesticides in water samples at different monitoring locations at river Satlej (2002-2003) Source: PPCB.

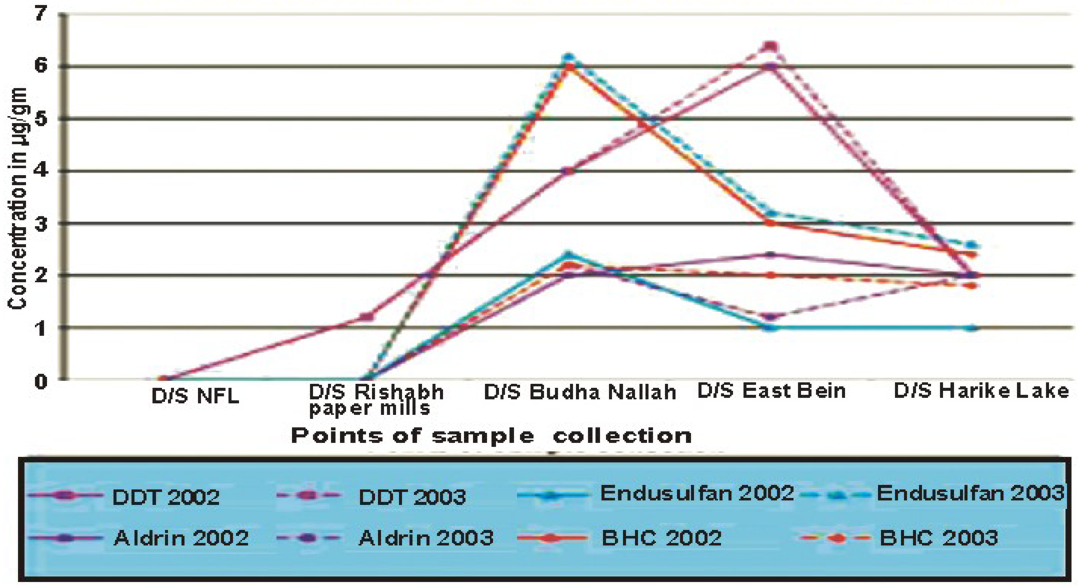


Fig:3.4 Concentration of pesticides in sediments at different monitoring locations at river Satlej (2002-2003) Source: PPCB

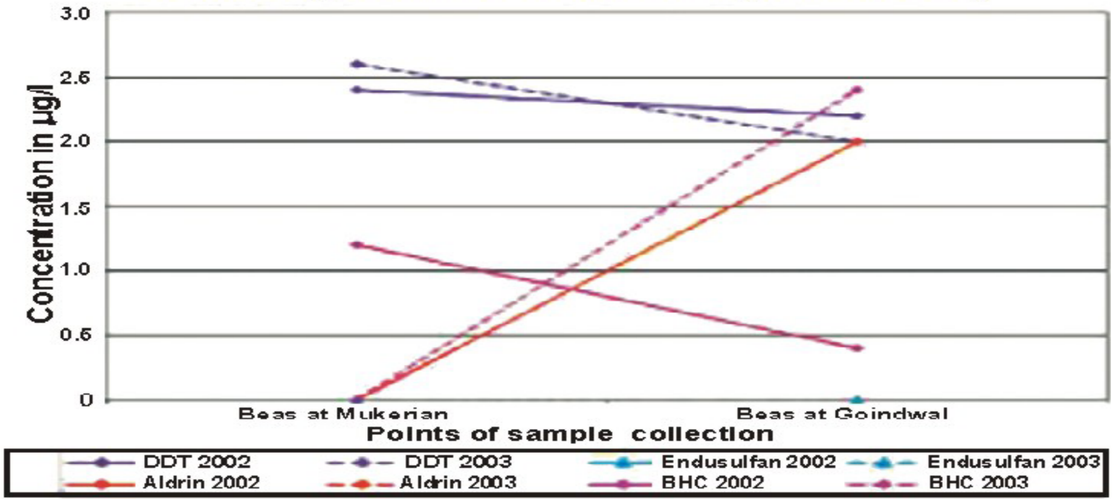
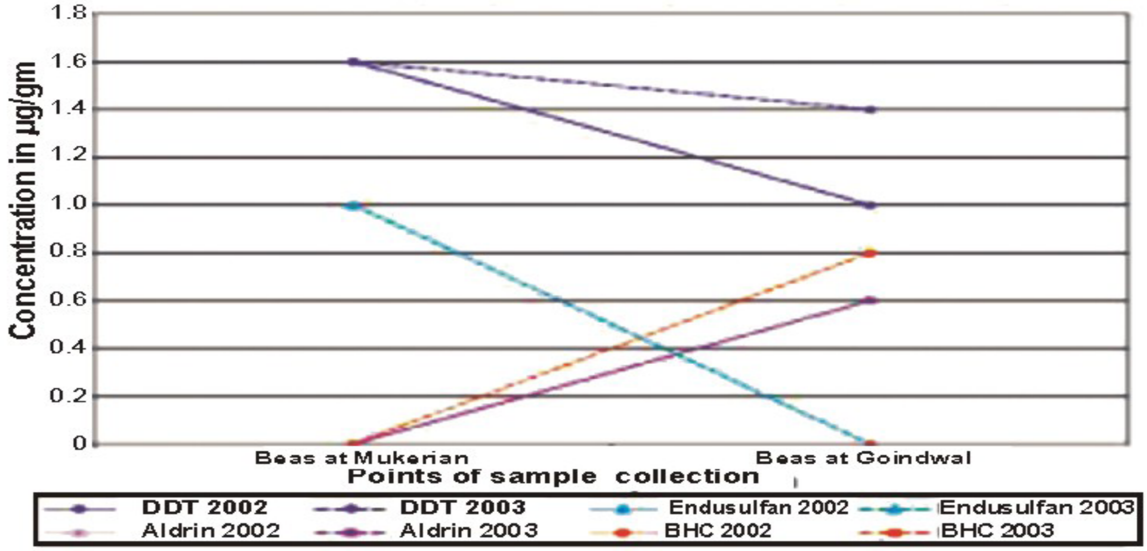


Fig: 3.5 Concentration of pesticides in water sample at different monitoring locations at river Beas (2002-2003) Source: PPCB.



F: 3.6 Concentration of pesticides in sediments at different monitoring locations at river Beas (2002-2003) Source: PPCB.

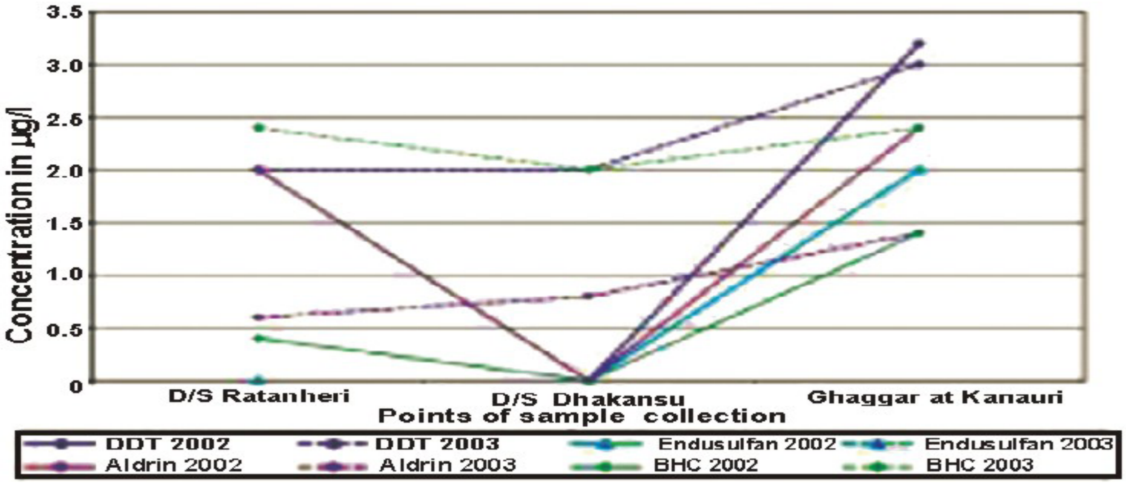


Fig :3.7 Concentration of pesticides in water sample at different monitoring locations at river Ghagger (2002-2003) Source: PPCB.

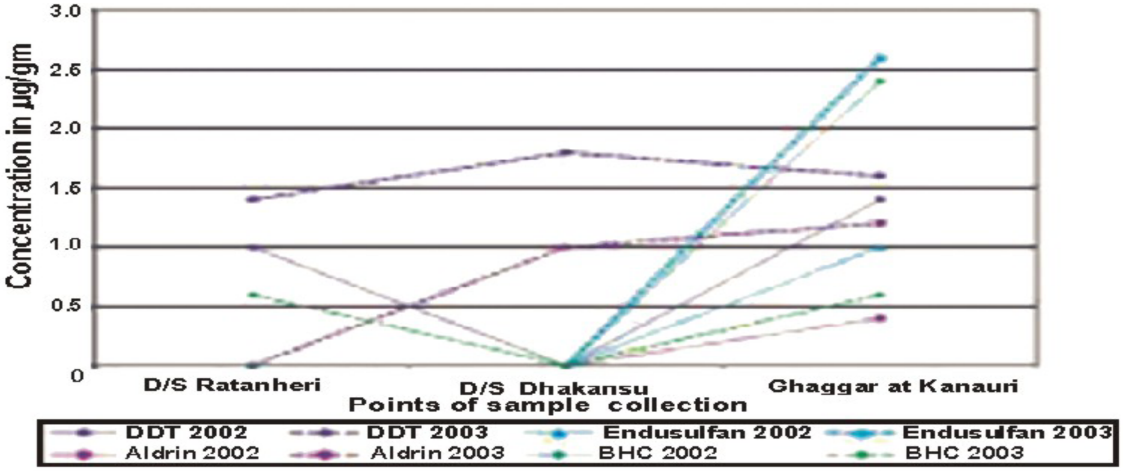


Fig: 3.8 Concentration of pesticides in sediments at different monitoring locations at river Ghagger (2002-2003) Source: PPCB.

Data indicates that the residues of pesticides are highest in river Sutlej. This could be primarily due to run off. Further, though DDT is banned in agricultural, however, it is still found in river water. Since this water is used for agricultural and human and cattle use in the state, it could causes adverse health impacts.

Pesticide is also affecting human health in Punjab

Some of the studies were conducted in Mahi, Nangal, Jajjal and Bollah village in Bathinda district and Dher village in the Roper district by Centre For Science And Environment, New Delhi ***(Mathura et.al, 2005)*** on analysis of pesticides in blood samples from villages of Punjab and result were found pesticides residues were present in very high level in human blood taken from five Punjab villages. The study tested 20 randomly selected blood samples which showed 15 to 605 times higher residues of certain persistence organ pesticides as compared to the samples in United States 6 to 12 types of pesticides residues were found. The average levels of monocrotophos in the blood samples (0.095 micro g/ gm) were found to be four times higher than the short-term exposure limits for humans, set by the world Health Organization and food and Agricultural organization.

Kalra and Chawala (1980) also conducted A Study in Occurrence of DDT and BHC (Benzenehexa Chloride) Residues in Human Milk in India. In this study, 75 samples of milk were collected from 75 lactating women residing in the state within a week after delivery.

Result indicated DDT and BHC residues in all 75 samples of human milk in Punjab was more than the level reported from USA, Canada, Europe and Australia, through the highest concentration of DDT of 4.07 mg/l in human milk was reported in Gutemala. BHC/HCH residues in milk were also reported to be higher than other countries of the world except Japan. DDT present at average levels of 0.5 mg/l in milk indicated an intake of 0.09 mg/kg/day of DDT, which is 18 times the ADI of 0.005 mg/kg/day recommended by WHO.

List of pesticides banned for use in agriculture Punjab state / India

Based on scientific study and feedback on certain national and international agencies some of the pesticides are banned in agricultural in Punjab state and whole India. These pesticides are given in Table **T.3.4**.

Sr.no.	Name of pesticides	Sr.no	Name of pesticides
1	Dibromochloropropane (DBCP)	10	Calciumcyanide
2	Endrin	11	Ethyl parathion
3	Pentachoronitrobenzene(PCNB	12	Ethyl mercury chloride
4	Pentachloropheno (PCP)	13	Menazon
5	Toxaphene	14	Sodium methane arsonate
6	Ethyl parathion	15	BHC/HCH
7	Chlordane	16	Phenyl Mercury acetate(PMA)
8	Heptachlor	17	Nicotine Sulphate
9	Aldrin	18	DDT

T.3.4: List of pesticides banned in Punjab (Source: Punjab Agricultural University Ludhiana 2004).

Effect of Pesticides on the health of children in Punjab

Kavitha Kuruganti 2003, her study-Evidence of the chronic effects of pesticides on the health of children and women in cotton growing areas in six Indian states. The main findings include cases of arrested development in children under 13, researchers with Greenpeace

India tested almost 900 children living in cotton-growing areas in six states for their developmental abilities, using a range of tests designed to measure analytical abilities, motor skills, concentration and memory. They found that children living in regions in which pesticides are widely used, performed significantly worse in various developmental abilities than children in a control group living elsewhere. The investigation reveals that children from regions as diverse as Tamil Nadu and Punjab, who have nothing in common but their exposure to pesticides, appear to share an inability to perform simple play-based exercises The six cotton belts in the country where the study was conducted apply high levels of extremely hazardous pesticides. Eighteen villages were chosen from six districts for the study. The researchers chose to study the impacts on the developmental abilities of children as they are particularly vulnerable to the impact of pesticides. The research selected at random 448 children aged 4-5 years and 451 children aged 9-13 for chronic exposure to pesticides – 899 children in all in the ‘study group’. For comparison, a total of 749 children were assessed from reference locations where pesticides were not used. In all other aspects the exposed and unexposed children were of a similar socio-economic and cultural background. The study was also able to document the more insidious effects of pesticides, not commonly known.

3. B ADVERSE EFFECT & ALTERNATIVES OF CHEMICAL PESTICIDES

3.B.1 Adverse effect of pesticides

The excessive use of chemical fertilizer like urea, DPK, NPK, etc and pesticides (insecticides and weedicide) have resulted in the disorders of endocrine glands e.g., thyroid, parathyroid, pituitary, kidneys and adrenals. The incidence of cancer, asthma and diseases of kidney, skin and digestive tract has increased by 20-25% in Punjab. Youngsters at the age of 25-30 are suffering from heart ailments and male infertility. Along-with suffering humanity, the soil is also sick with severe deficiency of micronutrients.

Decreasing carbon content of soil has resulted decrease in water & nutrient holding capacity. In addition organisms like bacteria, fungi and earthworms have disappeared. Furthermore, selenium levels in Punjab are very high at toxic level.

The food we eat, the water and milk we drink are contaminated with one or other chemicals. So much so the traces of BHC, endosulfan , DDT & HCH the banned pesticides have been found in the most safe & sacred mother's milk in many cases in Punjab.Due to use of Endosulfan in Punjab as in Kerala, the increase in the birth of mentally retarded children.

Kill even in Mother’s womb

Pesticides are known to negate the action of folic acid, vital for neural tube development. Pesticide residues in food can inhibit the intake of folic acid leading to birth of babies with congenital defects. The risk is higher if conceived at the time the Kharif and Rabi crops reach the market, a time when pesticide residue is very high.

Pesticides lead to male infertility

Exposure to pesticides and solvents could be contributing to falling sperm count and rising levels of male infertility.

Diseases:

Like - liver cancers testicular cancer and other evidence of chronic toxicity, mental disorders, neurological, congenital disorders, vomiting, headache, in the children’s as well as in adult peoples.

Creating awareness:

The fact that majority of the pesticide poisoning occurs in developing countries in spite of the lower consumption of pesticides ,shows the lack of awareness among the people of countries. So, there should be a greater emphasis on educating the people who work with these pesticides.

3.B.2 Precautions taken during application of Pesticides

Before spraying

- Identify the pest and ascertain the damage done.
- Use pesticide only if it has exceeded the economically injury level.
- Use only the recommended pesticide which is the least toxic.
- Read instructions manual of the pesticide and equipment.
- Check the spraying equipment and accessories which are to be used.
- Make sure that appropriate protective clothing is available and used.

During spraying

- Take only sufficient pesticide for the day's application from the store to the site.
- Do not transfer pesticides from original container and packing into the containers.
- Recheck the use instructions of pesticide and equipment.
- Never allow children or other unauthorized persons to be nearby during mixing, never leave pesticides unattended in the field.

After spraying

- Remaining pesticides left in the tank after spraying should be emptied and disposed off in pits dug on wasteland.
- Never empty the tank into irrigation canals or ponds.
- Never leave unused pesticides in sprayers.
- Always clean equipment properly. After use, oil it and then keep away in the store room.
- Do not use empty pesticide containers for any purpose.
- Crush and bury the containers preferably in a land filled dump.
- Clean buckets, sticks, measuring jars etc. used in preparing the spray solution.
- Remove and wash the protective clothing and footwear. Wash yourself well and put on clean cloth.

3.B.3 Alternatives of chemical Pesticides

- There are some practices by which we get rid of from using hazardous pesticides like organochlorine and organophosphate and carbamates for pest control. These practices are IPM Integrated Pest Management, Organic Farming, Bio pesticides and Crop diversification. These practices are extensively used by the farmers of Punjab.
- **Integrated Pest Management –IPM** is an ecofriendly approach which is an alternative available for the control of pests and this is technique to keep the pest population low .such as, mechanical and biological control with greater emphasis on use of crop rotation, bio-pesticides and pesticides for plant origin like neem formulation. The use of chemical pesticides is advised as last option only when pest population crosses the economical threshold level.

- **Organic farming –** system which avoids the use of synthetic inputs such as pesticides ,fertilizers,harnmones ,feed additives etc ,and to the maximum extent feasible,relies upon crop rotation, use of crop residues,animl manures ,off-farm organic wastes, mineral grade rock additives and biological system of nutrients mobilization and plant protection. The practice is gaining demand because growing awareness of health and environment issues in agriculture.
- **Bio pesticides and plant incorporated Protect ants** –are pesticides derived from natural materials such as animals, plants, bacteria, and certain minerals. They are safer than modern chemical pesticides. Bio pesticides includes neem and other plant based formulations like Repline, Neemmark, Indene, Guava family is also being used for alternative biological; pesticides. The strains of Bacillus thuringiensis most widely used plant are introduced in Bt cotton in Punjab
- **Crop Diversification-** refers to the shift from one particular cropping system to a varied and multi cropping system to stabilize farm income and protect our natural resources'. In Punjab mostly paddy-wheat cropping pattern are used. There is a urgent need to diversify into new areas like vegetables, fruits seeds pulses

CHAPTER -4

ADVANCED TREATMENT TECHNIQUES

4.1: Advanced Oxidation Process

Advanced oxidation process (AOPs) are used to oxidize complex organic consistutuents found in wastewater that are difficult to degrade biologically into simple end products. When chemical oxidation is used, it may not be necessary to oxidize completely a given compound or group of compounds. In many cases, partial oxidation is sufficient to render specific compound more amenable to subsequent biological treatment or to reduce their toxicity. The oxidation of specific compounds may be characterized by the extent of degradation of the final oxidation product ***(Rice 1996).***

4.1.1: Theory of Advanced Oxidation Process

Advanced oxidation processes typically involve the generation and use of hydroxyl radical, along with other common oxidants, that is given in the **T.4.1:** as shown, with exception of fluorine, hydroxyl radical is one of the most active oxidant.

Oxidizing agent	Electrochemical oxidation potential	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
Hydrochlorides	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

T.4.1: Comparison of oxidizing potential of various oxidizing agents (Source: Ozonia 1977)

As shown, with the exception of fluorine, the hydroxyl radical is one of the most active oxidant known. The hydroxyl radicals reacts with the dissolved constituents, initiating a series of oxidants reactions until the constituent are completely mineralized.

Advanced oxidation processes differ from the other treatment process because wastewater compounds are degraded rather than concentrated or transfer into diffused phase. Because secondary waste material are not generated, and there is no need to dispose of materials ***(Singer and Reckhow 1999).***

4.1.2: Technologies used to produce hydroxyl radicals (HO*)

At present, a variety of technologies are available to produce HO* in the aqueous phase. The various technologies are summarized in **T.4.2**, only ozone/ UV, ozone/hydrogen peroxide. Ozone/uv/hydrogen peroxide and hydrogen peroxide/UV are being used on a commercial scale ***(Rice 1996).***

Ozone based processes	**Non-ozone –based processes**
Ozone at elevated pH (8 to >10)	H_2O_2 + UV^b
Ozone + UV_{254}	H_2O_2 + UV+ Ferrous salts
Ozone + $H_2O_2{}^b$	Electron-beam irradiation
Ozone + UV_{254} + $H_2O_2{}^b$	Electro hydraulic cavitations
Ozone + TiO_2	Ultrasonic’s
Ozone + TiO_2 +H_2O_2	Nonthermal plasmas
Ozone +electron-beam irradiation	Pulsed corona discharges
Ozone + ultrasonic’s	Photocatalysis (UV+TiO_2)

T.4.2: Examples of technologies used to produce hydroxyl free radical (Source: Rice 1996)

Ozone/ UV- Production of the free radical HO* with UV light can be illustrated by the following reactions for the photolysis of ozone ***(Glaze and Kang 1990).***

$O_3 + UV \longrightarrow O_2 + O\ (1D)$

$O(^1D) + H_2O \longrightarrow HO^* + HO^*$ (in wet air)

$O(^1D) + H_2O \longrightarrow HO^* + HO^* \longrightarrow H_2O_2$ (in water)

The photolysis of ozone in a wet air results in the formation of hydrolysis radicals. In water, the photolysis of ozone leads to the formation of hydrogen peroxide because the photolysis of ozone leads to the formation of hydrogen peroxide, which is subsequent photolysed to form hydroxyl radical.

In air, the Ozone /UV process can be degrading compounds through direct ozonation, photolysis, or reaction with hydroxyl radical. The ozone /UV process is more effective when the compound of interest can be degraded through the absorption of the UV irradiation as well as through the reaction with the hydroxyl radicals.

Ozone/Hydrogen Peroxide – For compounds that do not adsorbed UV ,AOPs involving ozone/H_2O_2 may be more effective .Compounds in water such as trichloroethylene (TCE) and perchloroethylene (PCE) have been reduced significantly with AOPs using hydrogen peroxide and ozone to generate HO* ***(Karini et. al.,1997).***

The overall reaction for the production of hydroxyl radicals using hydrogen peroxide and ozone is as follows:

$H_2O_2 + 2\ O_2 \longrightarrow HO^* + HO^* + 3O_2$

Hydrogen Peroxide/ UV –Hydroxyl radicals are also formed when water containing H_2O_2 is exposed to UV light (200 to 280 nm).The following reaction can be used to describe the photolysis of H_2O_2

$H_2O_2 + UV \longrightarrow HO^* + HO^*$

4.1.3: Application of Advanced Oxidation Process

Practically any organic contaminant that is reactive with the hydroxyl radical can potentially be treated.

- A wide variety of organic and explosive contaminants are susceptible to destruction by UV/oxidation, including petroleum hydrocarbons.

- Chlorinated hydrocarbons used as industrial solvents and cleaners.
- Ordnance compounds such as TNT, RDX, and HMX.
- Chlorinated hydrocarbons that are resistant to biodegradation may be effectively treated by UV/oxidation.
- Easily oxidized organic compounds, such as those with double bonds (e.g., TCE, PCE, and vinyl chloride), as well as simple aromatic compounds (e.g., toluene, benzene, xylene, and phenol), are rapidly destroyed in UV/oxidation processes.

4.1.4: Limitations of UV/ Oxidation include:

- The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference). This factor can be more critical for UV/H_2O_2 than UV/O_3 (Turbidity does not affect direct chemical oxidation of the contaminant by H_2O_2 or O_3).
- Free radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical oxidizers may act as a scavenger.
- The aqueous stream to be treated by UV/oxidation should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves.
- When UV/O_3 is used on volatile organics such as TCA, the contaminants may be volatilized (e.g., "stripped") rather than destroyed. They would then have to be removed from the off-gas by activated carbon adsorption or catalytic oxidation.
- Costs may be higher than competing technologies because of energy requirements.
- Pre treatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves.
- Handling and storage of oxidizers require special safety precautions.

4.1.5: Advantage of Advanced Oxidation Processes

- Rapid reaction rates
- Potential to reduce toxicity and possibly complete mineralization of organics treated
- Does not concentrate waste for further treatment with methods such as membranes

- Does not produce materials that require further treatment such as "spent carbon" from activated carbon absorption
- Does not create sludge as with physical chemical process or biological processes (wasted biological sludge)
- Non selective pathway allows for the treatment of multiple organics at once
- Capital Intensive
- Complex chemistry must be tailored to specific application
- For some applications quenching of excess peroxide is required

4.2: Photocatalysis

Photo catalysis is the acceleration of a photoreaction in the presence of a catalyst or a change in the rate of chemical reactions or their generation under the action of light in the presence of substances -called photo catalysts- that absorb light quanta and are involved in the chemical transformations of the reaction participants. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photo generated catalysis the photo catalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals: ·OH) able to undergo secondary reactions. Its comprehension has been made possible ever since the discovery of water electrolysis by means of the titanium dioxide.

4.2.1: Principles of Photocatalysis

Photocatalysic destruction of organic compounds is based on semiconductor photochemistry. The most effective photo catalyst for this purpose is titanium dioxide. This is a non-toxic, material that is a constituent of toothpastes and many cosmetics. The Titania catalyst is illuminated by UV radiation with a wavelength sufficient to displace electrons from the valence band of the catalyst; for titanium dioxide this is below 387.5 nm. An electron/hole pair is produced on the semiconductor surface. The photo catalytic oxidation of an organic species often proceeds via adsorption of the pollutant on the surface of the catalyst, followed by direct subtraction of the pollutant's electrons by positively charged holes. Another possible way is oxidation with OH radicals, generated from water of the aqueous environment, which takes place at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the pollutant. And at last the organic compound can be completely degraded to carbon dioxide and water.

4.2.2: Photocatalyst : A substance that is able to produce, by absorption of light quanta, chemical transformations of the reaction participants, repeatedly coming with them into the intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions. The use of Photocatalysis is shown in the (**Fig: 4.1)** below:

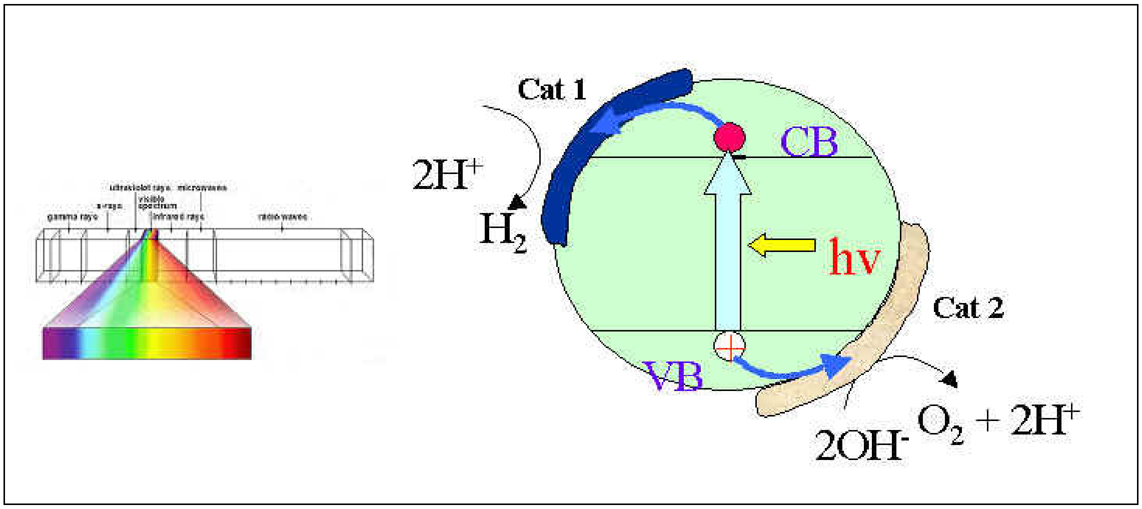


Fig: 4.1.The conversion of a photon into an electron-hole pair with a photo catalyst, this electron hole pair can be used for redox reactions like the splitting of water (Source: Fundamentals of Photocatalysis, 2004)

The photo catalyst uses a photon to excite an electron from the valence band to the conduction band: resulting in an excited state. The two protons, which are needed to generate hydrogen gas, can use the electrons that are excited in the photo catalyst. The hole in the valence band can be filled with an electron produced by the oxygen generation.

Additional catalysts can catalyse the two half-reactions. A requirement for the photo-catalyst is to have a band gap higher than 2.43 eV, which is the energy needed for the splitting of water. The goal is to split water into hydrogen and oxygen by the use of redox-reaction. Cat 1 facilitates hydrogen generation and cat 2 the oxygen creation. To enhance the speed of the reaction two things must happen. First, the association of protons needs to be quick and second; the electron generation needs to be high. The latter could be achieved by reducing the band gap to a wavelength where the intensity in sunlight is very high. The photon energy is converted to chemical energy accompanied with a largely positive change in the Gibbs free energy through water splitting as shown in **(Fig:4.2)**.This reaction is similar to photosynthesis by green plants because these are uphill reactions. Therefore, photo catalytic water splitting is regarded as an artificial photosynthesis.

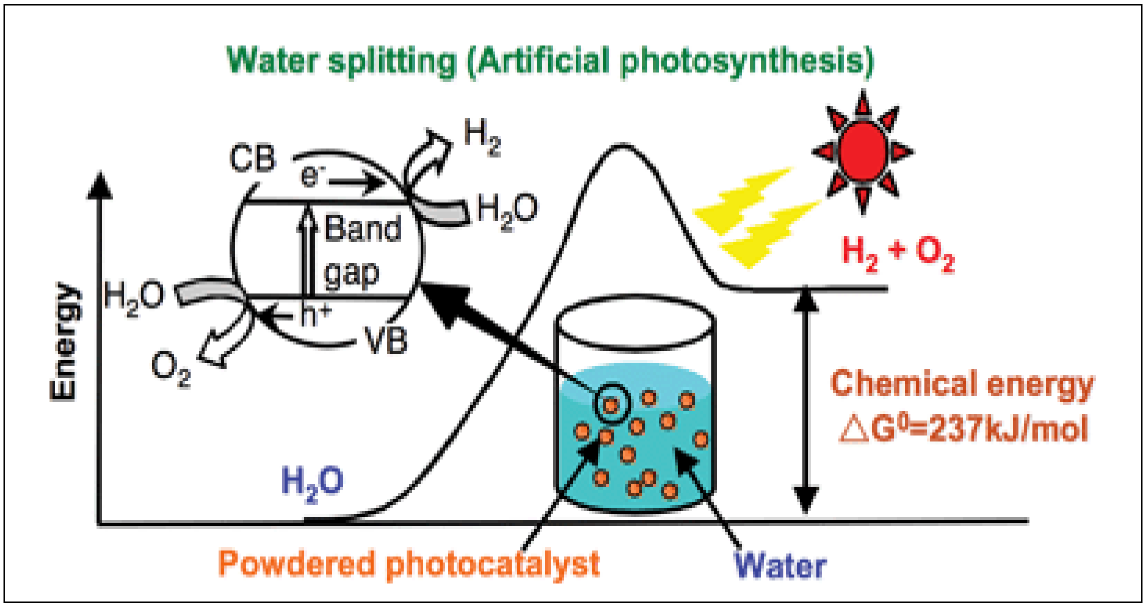


Fig: 4.2 Photosynthesis by green plants and photo catalytic water splitting as an artificial photosynthesis (Source: Fundamentals of Photocatalysis, 2004)

4.2.3: Properties of a good Photocatalyst

List of properties that are important for photo catalyst for water splitting-

- The band gap should be between 2.43 eV and 3.2 eV
- The valence band should be lower than the oxygen oxidation potential
- The conduction band should be higher than the hydrogen reduction potential
- The aid of a co-catalyst for hydrogen generation is necessary
- The photo catalyst must be able to split water in protons and hydroxyl anions
- The generation of water from molecular oxygen and hydrogen must be reduced
- Electron transport to the surface is necessary

4.2.4: How semiconductors works

Semiconductors are used as photo catalyst, when the semi conductors are exposed to UV lights, REDOX reaction will occur at the surface of the catalyst and generates $^{\bullet}OH$, Hydroxyl Radicals and O^{-}_{2}, Superoxide Ions. These 2 powerful oxidizing agents will then disintegrate and rearrange the structure of the VOCs and convert them into CO_2 and H_2O.

4.2.5: Types of Photocatalysis

4.2.5.1: Heterogenous Photocatalysis

Due to its high efficiency and the generation of harmless by products, the concept of the *Heterogeneous Photocatalysis* process has therefore caught the attention of many researchers and environmentalist all over the world. Photocatalysis aided by semiconductor, Titanium dioxide nanoparticles is used in removing the organic chemicals which occur as pollutants in wastewater effluents from industrial and domestic sources. This process is a combination of heterogeneous catalysis and solar technology. The Photo catalytic process breaks down the compounds such as alcohols, carboxylic acids, amines, herbicides and aldehydes into carbon dioxide, water and simple mineral acids. The main advantage of Photocatalysis is that there is no further requirement for secondary disposal methods ***(Abhijit V. Jadhav 2005).***

Heterogeneous Photocatalysis using semiconductor oxides has demonstrated to be very effective to treat pollutants both in gas and in liquid phase ***(Augugliaro et al 2006)***. The photo excitation of semiconductor particles promotes an electron from the valence band to the conduction band thus leaving an electron deficiency or hole in the valence band; in this way, electron/hole pairs are generated. Both reductive and oxidative processes can occur at/or near the surface of the photo excited semiconductor particle. In aerated aqueous suspensions, oxygen is able to scavenge conduction band electrons forming superoxide ions ($O_2^{\bullet-}$) and its protonated form, the hydroperoxyl radical ($HO_2^{\bullet}$):

$O_2 + e^- \rightarrow O_2^{\ \bullet}$ (1)

$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$ (2)

In this way, electron/hole recombination can be effectively prevented and lifetime of holes is prolonged $HO_2^{\bullet}$ can lead to the formation of H_2O_2:

$HO_2^{\bullet} + e^- \rightarrow HO_2$ (3)

$HO_2^- + H^+ \rightarrow H_2O_2$ (4)

Photogenerated holes can react with adsorbed water molecules (or hydroxide anions) to give hydroxyl radicals:

$H_2O + h+ \rightarrow HO\bullet + H+$ (5)

Superoxide anion can also act as an oxidant. The whole process can end in the complete mineralization of organic compounds.

4.2.5.2: Homogenous Photocatalysis

In homogenous Photocatalysis, the reaction takes place in similar or homogenous phases like liquid – liquid phases .examples are dye with soluble metal catalyst.

A number of pesticides have been tested with organic dye and $FeC1_3$ photo catalysts. All of the pesticides could be degraded with FeCla-H_20_2, but only some with Methylene blue as given in **(T. 4.3)**. It was thought that it might be possible to enhance the catalysis of $FeOH^{++}$ by complexing it with an organic dye that extended the spectral range of absorption ***(Irving Spiewak et. al, 1998).***

Compound	**Oxygen** **Methylene blue ,Alkaline pH**	**H_20_2** **Ferric chloride ,pH 3 to 4**
Bromacil	Rapidly degraded	Readily degraded
Tribufos	No reaction	Rapidly degraded by $H_2 0_2$ dark. Degraded by $FeC1_3$ + sun
Atrazine	No reaction	Readily degraded
Lindane	No reaction	Degraded

T.4.3: **Summary of insecticide behaviour in sunlight. Methylene blue vs. ferric chloride catalyst Source: International journal of environmental health Vol. 8: 223-239**

4.3: Sonication / Ultrasonic's

4.3.1: Description of technology

Ultrasonic technology may be used for water and wastewater treatment as an advanced oxidation process. Application of this technology, leads to the decomposition of many organic compounds during cavitations process.

Sonication of liquid media results in the formation of micro bubbles that grow to a critical size and then implode. Temperatures at the collapsing bubble interface are about 5,000 ^{o}K and pressures are near 500 atmospheres, but the bulk solution remains near ambient conditions. In these highly reactive conditions, hydroxyl radicals ($^{-}$OH) and hydrogen ions (H^{-}) are generated; they are very effective at degrading organic compounds. If organic compounds are present in the water, they are rapidly destroyed, either directly or by reacting with the free radicals. The intensity of cavity implosion, and hence the nature of the reactions involved, can be controlled by process parameters such as the ultrasonic frequency, ultrasonic intensity per unit volume of liquid medium, static pressure, choice of ambient gas, and addition of oxidants (e.g., H_2O_2, O_3).

Cavitation:

The cavitation phenomenon includes formation of bubbles , nucleation ,growth of the bubbles .When liquid is exposed to the high frequency radiation both the physical and chemical phenomenon take place., additional energy which is present in the vicinity of gas bubbles and in the surrounding medium the temperature and pressures increases tremendously respectively 2000 to 5000 ^{0}C and 1800 atm, this condition remains for very short time interval but this high temperature and pressure is sufficient for cleaning the impurities which is present in the sample water. Cavitation, induced by ultrasound at low frequencies, is an effective means for the disintegration of bacterial cells. Two effects can be observed: At low ultrasound doses bacteria flocs can be declumped by mechanical shear stresses, and at increased doses ultrasound cavitation has an impact on the cell walls such that they are broken. This ultrasonic advanced treatment is used for the treatment of municipal wastewater ***(U. Neis and T. Blume 2002).***

4.3.2: Wastewater treatment by Sonication

Cavitation for the occurrence of the reaction can be achieved by thermal, photochemical, electrochemical, and sonochemical activation. All these techniques can be considered as supplying energy to make an active oxidizable species of the pollutants. Sonication involves sonochemistry which is basically a term related to the effect of ultrasonic waves on the reactants ***(Panditt et. al, 2000).***

Basics of Sonochemistry:

l. Transducers are used for the generation of ultrasound and they are liquid driven or magnetostrictive or piezoelectric transducers. It is only ultrasound that is useful for chemical reactions.

2. Similar to the transmission of the normal sound waves, in ultrasound (frequency > 16 KHz) during the rarefaction stage of the wave, the liquid molecules are torn apart causing cavitation to occur i.e. formation of voids. These spots or cavities violently collapse during the next compression cycle. Thus propagation of ultrasonic waves in the liquid promotes the formation of cavitation bubbles which can grow and implode under the periodic variation of the pressure fields.

4.3.2.1: Waste water treatment

When ultrasound is applied to effluent, water undergoes thermal dissociation to H atoms and OH radicals. OH is highly reactive and can oxidise almost all contaminants in water. This primary oxidation is the reason for the degradation of contaminants in water. Sonochemical reactions are normally characterised by the simultaneous occurrence of pyrolysis and radical reactions, especially at high solute concentrations. Volatile solutes undergo direct pyrolysis reactions within the gas phase of the collapsing bubbles or within the hot interfacial (cavity-liquid) region. Phenols, chloro-phenol, nitro phenol, parathion, etc. are among a few regularly observed contaminants in an industrial effluent, which are known to get degraded by the cavitation phenomenon.Degradation change with the change in the intensity of ultrasound, concentration of the contaminant in water etc. An unanticipated advantage is that sonication also kills some microorganisms and hence disinfects water.

4.3.2.2: Concept of decontamination

The reaction that occurs during the photo catalyst mediated destruction of wastewater is a radical reaction and the radical formation occurs due to the activation energy supplied by the highly energetic UV radiation to the catalyst surface and the water molecules in the effluent. A number of semiconductor oxides can be used as catalysts for this particular purpose. The semiconductor oxide molecules on illumination with radiation having energy greater than its optical band gap transfers an electron to the conduction band leaving a hole in the valence band. At the solid-liquid interface the electron transfer occurs either from the conduction band to an acceptor in the solution or from a donor in solution to the valence band. These processes compete with the recombination of electron and hole to produce thermal energy, which is not useful for decontamination. In the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination.

The valence band holes are powerful oxidants (1.0 to 3.5 V) while conduction band electrons are good reductants (0.5 to - 1.5 eV). This eventually leads to photocatalytic redox processes ultimately leading to the destruction of the organic molecule. The most important thing that can lead to the reaction is the reacting substance remaining in contact with the surface of the catalyst.

4.3.3: Advantages

The ultrasonic treatment of waste is quite novel.

- Reduce waste quantities
- Achieve a better dewater ability
- Provoke a release of soluble chemical oxygen demand (COD) from the bio solids, preferably transformed into biodegradable organics
- Destroy the filamentous microorganisms responsible for sludge bulking
- Chemically free

4.3.4: Applications:

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

- 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 ***(Grewell 2007).***
- Removal of pollutant s from dye industry and textile industry and others organic pollutants like pesticides and hazardous metals.
- Cleaning of drinking water, as well as contaminated soil.
- Used for the dewatering of sludge and reducing the faecal coli form.

CHAPTER -5

REVIEW OF LITERATURE

Overview

Organophosphate & Organ chlorine pesticides (OCP) have been used in agriculture and livestock for quite a long time to control a variety of crop pests and animal ectoparasites. They have also been employed to combat vectors of malaria and some other deadly diseases of human being. Of late, some of the compounds belonging to OCPs like aldrin, dieldrin, heptachlor, DDT, HCH, etc. which are also important constituents of the toxic group known persistent organic pollutants (POPs), have been banned or restricted. The OCPs owing to their high persistence nature due to chemical stability and lipophilic character accumulate in different environmental compartments and in food chain thus causing elevated contamination in human body. These residues bio concentrate in lipid rich tissues according to equilibrium pattern of internal transport and lipid tissue content and decline at a very slow rate even after sources of contamination are eliminated. The intake of contaminated feed and fodder by the milch animals is the main source of entry of pesticides in to the animal body which ultimately results in the contamination of milk, meat, etc. consumed by human being.

5.1. Estimation of pesticides

(Subir K. Nag Mukesh K. Raikwar 2008) bovine milk samples (325) were collected at random from different places covering UP and MP districts of Bundelkhand region of India like Jhansi, Banda, Gwalior,etc. Sample were taken afresh in the morning in glass bottles, kept in ice thermocol box during transport and stored in deep fridge in the laboratory before analysis. The result of the study revealed, contamination of milk from pesticide residues was observed in number of contaminated samples which exceed the tolerance level.

Thus human body also gets contaminated. There are number of reports available about the occurrence of organ chlorine pesticide residues in milk from different parts of India as well as abroad. Milk has a very special position in the diet of infants, children and elderly for whom it is considered as a perfect natural food. Being a fat rich food it is an important source of OCP accumulation and hence one of the convenient food stuff for measuring the persistent OCPs.

Pesticides are of great concern to the Indian consumer as well as other countries consumers. While the use of pesticides and other agrochemicals has increased the availability of fruits and vegetables, some research indicates the residues of these compounds may constitute a health hazard. Pesticides cause's diseases in children, reproductive disorders in men, and breast cancer in women contribute to these concerns. The issues involved are complex, and the literatures dealing with the topic are as follows. Monitoring of 80 winter vegetable samples during 1997–1998 for pesticidal contamination was carried out on GC-ECD and GC-NPD systems with capillary columns following multiresidue analytical technique. More extensive monitoring studies covering all vegetable crops from different agro-climatic regions of the state are carried out to know exact level of pesticidal contamination, which may serve as basis for future policy on chemical use ***(Beena Kumari 2003).***

This problem is more serious in case of vegetables as these are often consumed either raw or without much processing or storage. Having global existence, organ chlorine insecticide residues have been reported from each and every environmental commodity such as water, vegetables, milk etc***. (Kumari et al., 1996)***

This article presents the development of a multiresidue method for the estimation of 30 insecticides, 15 organ chlorine insecticides and 6 organophosphorus insecticides, 9 synthetic Pyrethroids and 2 herbicides and their quantification in vegetables. The monitoring study indicates that all the vegetable samples were contaminated with pesticides, only 31% of the samples contained pesticides above the prescribed tolerance limit. Vegetables are a main source of diet in the Indian sub-continent. The average Indian diet constitutes of about 150–250 g of vegetables in the total meal per day. Literature reveals that vegetables are contaminated ***(Elliion et al., 2000).***

One study reported a for determination of pesticide residues in Cauliflower. Cauliflower sprayed with, 4 different pesticides (diazinon, malathion, chlorpyrifos and cypermethrin) at recommended dose and double of recommended dose were analyzed for their residual contents and found that is highly contaminated by pesticides ***(Nazneen Afrin and Mohammad 2009).***

In Agricultural, cereal crops are most contaminated by several pesticides, by bioaccumulation and magnification property, it enters into the food chain and causes the potential hazards.

Increased use of chemicals on vegetables started gaining momentum and continued its up-trend in Bangladesh. Wide spread use of pesticides in agriculture concern of residue accumulation, which may remain in food and agricultural environment causing concern of human health and risking ecological balance. The major crops grown in the country are rice, wheat, jute, potato, sugarcane, vegetables and tea.

Wheat is the most important cereal crop and constitutes the main component of millions of heads world over. It is frequently stored for long periods of time with consequent risk of heavy insect infestation. ***(Praveen Z.et al., 2007)*** detect the organophosphorus pesticides such as Malathion, chlorpyriphos, bifenthrin and permethrin and Synthetic Pyrethroids in wheat with the help of extraction methods. Similar studies were carried out by ***(Daglish & Nayak 2006).***

Fresh fruit and vegetables have been identified as a significant source of pathogens and chemical contaminants. Now these days we are consuming food like vegetables, grains, milks all these are contaminated by the excessive exposure of pesticides in direct and indirect way. Residues of pesticides in dietary form ,accumulate in the tissues of human being and animals causes many disease like neurological ,congenital defect, headache ,cancers and eye irritation and sometimes exposures leads to the death .Some of the researchers work in this field that are as follows ***(Solomon R.D & Subramaniam K., 2006)*** analysed the blood sample of patient who are in direct exposure to pesticides DDE and BHC , high concentrations of both BHC & DDE were observed in the serum samples of the people who had direct exposure to the pesticides, namely agriculturalists and public health workers with few exceptions. The pesticide residue concentration in serum ranges from 0.006 to 0.130 ppm for BHC and 0.002 to 0.033 ppm for DDE.

Soil and groundwater pollution are the main environmental effects of pesticides. However, there are evidences that many species of insects, mammals and birds have been affected. Pesticides in soils become toxic to arthropods, earthworms, fungi, bacteria, and protozoa which are vital to ecosystems, because they dominate both the structure and function of natural system.

(Andrade et.al 2007) reported the Concentrations of lindane, DDT, dicofol, and related side products or degradation products were determined at depths of 0 to 20, 20 to 60 and 60 to 100 cm along a 300-m transect running between the land infill and a nearby river.

As the pesticide contaminates the soil because of persistence and bioaccumulation property, these get accumulate and become more toxic and causes impacts. Pesticide exposure can have chronic and acute impacts on human health. Long term low dose exposure to pesticide causes immune suppression, hormonal disruption, diminished intelligence, reproductive abnormalities and cancer ***(Gupta, 2004).***

Another problem which occurs due to pesticide is the conversion of pesticides into the obsolete form, which may even show more harmful effects than the former. When the pesticides are not used within the prescribed time of their efficacy, they become obsolete. **"Obsolete pesticides"** are defined as those pesticides that can no longer be used for their intended purpose or wanted to be used and therefore must be disposed off. They are decomposed into other chemical components, which are sometimes even more toxic than the original pesticides.

In case of obsolete pesticide lack of health related studies and very limited studies on environmental contamination by obsolete pesticides led to undertake this study which focuses on health and environmental impacts of obsolete pesticides stored in a warehouse at Amlekhgunj, Bara district, Nepal, ***(Binod P Shah and Bhupendra Devkota 2009).***

Pesticide detected ***(Moraes et.al, 2003)*** at all 7 sites surveyed residues of a total of 27 pesticides or metabolites were found in water and/or sediment samples and fish have accumulated some of the most persistent of these residues. Several pesticides in water were above levels for drinking water recommended by the Europeans society. In case of drinking water, sample extraction with methyl chloride, analysis was directly carried out without further treatment using GC. Recoveries of six OPs at spiked level of 0.50, 2.50 and 4.50 microgram/ litre ranged from 88 to 104 %. These Ops were reproducibly detected well below the maximum limits (MRLs) of EPA method 525 and European Union regulation for pesticide residue in drinking water.

In case of bottled drinking water (BDW) in Mexico City. The results of 36 samples (1.5 and 19 L presentations, 18 samples, respectively) showed the presence of seven pesticides (HCH isomers, heptachlor, aldrin, and -DDE) in bottled water compared with the drinking water standards set by EPA, and World Health Organization. The concentrations of the majority of organic chlorine pesticides were within drinking water standards (0.01 mg/ml). It is important for monitoring drinking bottled water for protecting human health ***(Gilberto Dıaz.et.al; 2008).***

A method for determination of a selected group of pesticides in water (tap and ground water) was developed using liquid chromatography-(electro spray ionization)-mass spectrometry. The pesticides dimethoate, carbaryl, simazine, atrazine, ametryne, tebuthiuron, diuron and linuron were isolated using liquid-liquid extraction with dichloromethane and analyzed on a reversed phase column, C-18, with gradient elution at flow rate of 1 mL./ min. Recoveries ranged from 89% to 112%) for tap water and from 76% to 98% for ground water ***(Lan zau K., 2004).***

For extraction of organics chlorinated pesticide in fish samples by GC gas chromatography ***(Larry J. Schmidt, 1995)*** .Extraction method was used in the Pesticide analysis. The best extraction efficiency and clearest extracts are obtained. The analyses were carried out by capillary gas chromatography with nitrogen and phosphorus detection; found that the fishes are also contaminated with pesticides.

A new multiresidue extraction technique was used to determine incurred chlorinated hydrocarbon pesticide residues in various fish species sampled at 2 locations along the Tensas River in Louisiana. Residue levels of total DDT (combined DDT, DDE, and DDD levels) in fish muscle fillets from paired samples ranged from 0.2 to 3.9 ppm on a wet weight basis ***(Lott H. and Barker S. 1992).***

Organ chlorine Insecticide Residues of DDT and HCH were in Water from Five Lakes Bhimtal, Sattal, Khurpatal, Naukuchiatal and Nainital of Nainital (U. P.), India ***(Sharma V. P, 1997)*** because of chemical nature, they became major environmental pollutions .Several studies were conducted on Organo chlorine insecticide contamination in lakes and water reservoirs from other part of the world.

Organo chlorine pesticides (OCPs) are known to be persistent and bio accumulative toxicants that may cause reproductive impairments in wildlife as well as human. The effectiveness of the treatment process for the removal of pesticides in the final water supplies in Delhi has been evaluated ***(Sukumar Devotta 2007)*** Samples was collected during 2000–2005 from five water treatment plants (WTPs).Analysed the pesticides, which are more commonly present in treated drinking water. In most of the treatment plants, the concentrations of lindane, total endosulphan and total DDT were significantly less in the finished water.

M. Saglam (2009) investigated the ground water quality of a typical agricultural area of the gean Region, in the Izmir Districts, concerning nitrate and pesticide pollution. Elevated nitrate and pesticide concentrations in drinking water present a potential risk to public health. The ground water was sampled from wells that are used as a local drinking water supply and for the irrigation of farms. The results indicate that the ground water of these areas has started contaminated by nitrate because of fertilizer use. At one location, the maximum contamination levels for pesticides in drinking water were exceeded by three pesticides (propargit, endosulphan, fenitrothion).

The method was applied to real samples. Tap water was collected at the laboratory in Ghent, Belgium. Ground water was collected from an artesian well, also in Belgium. Pesticides that belong to the triazines class (simazine and atrazine) were detected in tap water but no pesticides were found in the ground water ***(Sonia C. N. Queiroz 2004).***

The insecticides contamination is most popular in water bodies like rivers, ponds, reservoirs and hence the accumulation of pesticide in water bodies creates many hazardous problems to aquatic life and near survivals. Surface water samples collected by dip sampling method from farm ponds/collection wells and other irrigation sources ***(K. Bhuvaneswari, A. Regupathy 2006)*** the per cent occurrence of insecticide residues observed in the samples was 60.6, 56.1, 57.6 and 52.3 for carbofuran, quinalphos, phorate and fenvalerate, respectively in same region. Most of the soil applied insecticides pollute groundwater by runoff and leaching and the severity depends on land characters like slope and texture, climatic factor like rainfall intensity and physico-chemical properties of pesticides (***Flury et. al., 1995).***

Since it is known that pesticides used in agricultural practices may appear in the rain because of the volatilization of compounds applied on soil and plant. Contamination of air and rain may have consequences for the ecotoxicological and toxicological judgment of pesticides because they may be widely distributed and may affect all ecosystem compartments (i.e. water, drinking water) but if the polluted water is used then it brings disease and death to those who drink it and other forms of life that needs to survive. Besides the other pollutants, pesticide residues are also one of the dominant contaminant of water as lot of pesticides are used to combat the insect–pest complex of agriculture and other fields related to health programme. ***(Beena Kumari &T. S. Kathpal 2007)*** analysed the presence of pesticides residues in rain water by GC technique, detected 13 pesticide in the rain water samples ,found DDT in the range of 0.041–7.060 ppb Synthetic Pyrethroids were present ranging from 0.100 to 1.000 µg /l and organophosphates in the range of 0.050–4.000 µg /l.

Pesticides are prone to contaminate the soil because of their property, persistence in soil. Persistence is measured as the time it takes for half of the initial amount of a pesticide to breakdown. if it is also very soluble in water and the conditions are right, it can move rapidly through certain soils. In contrast, very persistent pesticides may have other properties which limit their potential for movement throughout the environment. Many of the chlorinated hydrocarbon pesticides are very persistent and slow to breakdown but also very water insoluble and tend not to move down through the soil into groundwater. They can, however, become problems in other ways since they remain on the surface for a long time and contaminate the soil.

Today there has been an increased concern on the safety of the applied disposal method and on the soil contamination close to these places. ***(Hourdakis et.al, 2000)*** were analysed for the presence of dimethoate, dinocap, mevinphos, diazinon, and parathion residues, while the samples from Messinia were analysed for aldrin, dieldrin, gamma-BHC (lindane), parathion, and DDT residues from disposal site.

5.2. Treatment by Advanced Oxidation Process

For the oxidation of pollutants, a series of researcher used advanced oxidation for the degradation of pollutants and this process involves different techniques that are given below - AOPs involving Photocatalysis, sonication or a combination of both processes can be divided into six categories:

– Photolysis: the use UV irradiation (either UV-A, B or C) without the presence of any catalyst, to irradiate a polluted aqueous solution. This method does not fully decompose the organic pollutant molecule but instead generates intermediates from the pollutant molecules, which could be more hazardous than the parent pollutant molecule.

– Photocatalysis: the use of a photo catalyst (anatase-type TiO_2 or ZnO) in the presence of UV irradiation (usually UV-A with a wavelength 315–400 nm).

– Sonolysis: the use of ultrasonic irradiation without the presence of any catalyst, in order to generate hydroxyl radicals in an aqueous system. This method suffers the same drawbacks as the photolysis method.

– Sonocatalysis: the use of a photo catalyst TiO_2 (researchers has shown that rutile-type demonstrates better catalytic effect as compare to anatase-type) in the presence of ultrasonic irradiation but without the presence of UV irradiation.

– Sonophotolysis: the use of ultrasonic sound waves and ultraviolet irradiation simultaneously without the presence of any type of catalyst.

– Sonophotocatalysis: the use of a photo catalyst TiO_2 in the presence of ultrasonic and UV irradiation.

In advanced oxidation process, Sonophotocatalysis is another technique that is used for degradation of organic constitutes. Sonophotocatalysis involves the use of a combination of ultrasonic sound waves, ultraviolet radiation and a semiconductor photo catalyst to enhance a chemical reaction by the formation of free radicals in aqueous systems. Researchers have used sonophotocatalysis in a variety of investigations i.e. from water decontamination to direct pollutant degradation.

This degradation process provides an excellent opportunity to reduce reaction time and the amount of reagents used without the need for extreme physical conditions. Given its advantages, the sonophotocatalysis process has a futuristic application from an engineering and fundamental aspect in commercial applications.

(Joseph et.al, 2009) stated in their research paper, use of sonophotocatalysis as an emerging treatment process improves the overall efficiency of the AOPs and chemical reaction kinetics and reduces the need of employing extreme physical conditions. Sonophotocatalysis, further contributes to the effectiveness of photo catalytic 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. The overall sonophotocatalysis effect is also greater than the additive effects of the two processes.

Composition and morphology of the photo catalyst are not adversely affected during the sonophotocatalysis treatment. In fact, particle disaggregation induced by the ultrasound may actually enhance surface area of the photo catalyst. The synergistic effect of ultrasound and UV irradiation plus the further synergy between the catalyst support and photo catalyst, increases free radicals formation in the aqueous medium, increases the formation of bubble cavities, accelerate and facilitate mass transfer of pollutant molecules onto the photo catalyst surface as well as remove any impurities from its surface. Increased treatment cost associated by increased energy consumption can be offset by the reduced treatment time required. Sonophotocatalysis appears to be the most promising process for commercially viable decontamination process. The replacement of UV irradiation with sunlight should also be the goal of an efficient sonophotocatalysis system. This would drastically reduce the cost factor for this type of AOP treatment.

Photocatalysis Oxidation (UV/TiO_2)

(Leyva et.al, 1999) The photo catalytic degradation of herbicide pure Paraquat (1, l'-dimethyl-4, 4'-bipyridinium dichloride) aqueous solutions with UV light over titanium oxide was investigated. Experimental results have confirmed that Paraquat is slowly degraded by direct photolysis in the presence of dissolved oxygen. Addition of TiO_2 to the reaction system substantially increases the initial rate of reaction and the overall conversion of Paraquat. Complete photo catalytic degradation of Paraquat at high pH values was found to occur in less than three hours of reaction.

The heterogeneous photo catalytic degradation process is also one of the most popular emerging processes between the researchers for the treatment of organic pollutant.

In One study ***(Evgenidou et.al, 2007)*** the heterogeneous photo catalytic degradation of prometryn using TiO_2 as photo catalyst was investigated. They evaluated the kinetics of the pesticide disappearance, compared the photo catalytic efficiency of two different types of TiO_2 and examined the influence of various parameters such as initial concentration of pesticide or catalyst and presence of oxidants (H_2O_2 and K_2S_2O8). The experiments were carried out in a 500 ml Pyrex UV reactor equipped with a 125 W high-pressure mercury lamp surrounded by a Pyrex filter blocking wavelengths below 290 nm. A synergistic effect was observed when an oxidant was added in the TiO2 suspensions increasing the reaction rate of photo degradation.

(Madani et.al, 2006) carried the practical elimination of pesticides from water by Photocatalysis by using two commercial Titania photo catalysts (Degussa P25 (50 m^2/g) and Millennium PC500 (340 m^2/g)) and by choosing diuron as a model molecule. These two catalysts have been tested and compared in suspension in a slurry reactor. Their activities have been based on the rates of diuron disappearance diuron. In particular, comparisons have been made on their initial activities, which is independent of the influence of intermediates formed. Under identical conditions, Degussa P25 appeared substantially more active than Millennium PC500. However, since the final filtration of Titania powders in suspension for the release of cleaned water and the recovery of the catalysts is a tedious process, Titania has been successfully deposited on flexible photo-inert supports to be easily removed and recycled.

(Gunlazuardi 2005) The degradation of pentachlorophenol solely by UV light (photolysis) was observed due to dechlorination of pentachlorophenol molecules, and aromatic intermediate remained. The aromatic intermediate could be further degraded in the presence of TiO_2 (anatase) supported on titanium and UV light (Photocatalysis). Both in photolysis and Photocatalysis the dechlorination event were evidenced.

Similar study was also carried out by the ***(Emmanuelle 2003)*** They had investigated photo catalytic degradations of six sulfonylurea herbicides in aqueous solutions containing TiO_2 suspensions as photo catalyst, in order to assess influence of various parameters, such as adsorption, initial concentration and photon flux on the photo catalytic process. Resulted the adsorption is an important parameter controlling the apparent kinetic order of the degradation (either one in the case of associative adsorption or a half in the case of dissociative adsorption). A higher efficiency is observed under the lower photon fluxes, the limiting factor being the electron–hole pair recombination.

(Yongsong Cao et.al, 2005) In this study, the direct photolysis and the photo catalytic degradations of chlorfenapyr in TiO_2 suspensions with and without the use of hydrogen peroxide were studied using two different monochromatic UV irradiations (300 and 350 nm). Photolysis reactions were slow, and the corresponding Photocatalysis rates were increased by about 2.5 and 3 times in the presence of TiO_2 at 300 and 350 nm of UV, respectively. Photo catalytic rates were increased with the pH at neutral to alkaline ranges because of the increase of hydroxide ions. However, the reaction was gradually retarded at the neutral medium. The half times of degradation ($t1/2$) were 13.7, 16.2, 16.2, 10.7 and 8.7 min, respectively, at pH 4, 6, 7, 9 and 11. Thus, chlorfenapyr was less stable in acid and alkaline environments, and relatively more stable at neutral conditions. The effect of temperature is helpful to the photo catalytic degradation of chlorfenapyr. The photo catalytic degradation rates were found to increase with TiO_2 dosages, and the reaction was retarded at higher TiO_2 dosages. The fastest degradation occurred when 1200 mg L−1 TiO_2 was used, the rate increased slowly with increasing catalyst concentration up to 800 mg L−1 and more rapidly when the concentration was increased from 800 to 1200 mg L−1, and decreased at 1600 mg L−1. A much faster degradation rate at lower chlorfenapyr concentrations was achieved. The results of H_2O_2-assisted Photocatalysis experiments showed that a low H_2O_2 dosage in Photocatalysis would enhance the degradation rate of chlorfenapyr; however, an overdose of H_2O_2 will retard the rate because of the expenditure of hydroxyl radicals.

(Biljana et.al, 2004) **-**The kinetics of the photo catalytic degradation of 3-amino-2-chloropyridine, as a model compound for pyridine containing pesticides, in UV illuminated aqueous suspensions of TiO_2 were investigated. It was found that mineralization to carbon dioxide, water, chloride, ammonia, and nitrate takes place during the process. The rate of degradation was studied by HPLC, ion chromatography and UV spectrometry, as well as by continuous potentiometric measurement of the rate of chloride generation and the pH change of the medium. It was found that the reaction in the investigated concentration range is of the zero-order in respect to 3-amino-2-chloropyridine degradation with the reaction rate constant 8.9×10−6 mol/(dm^3/min) and adsorption coefficient 1.2×104 dm^3/mol. HPLC analysis indicated that very few pyridine containing intermediates at low concentrations are formed during the process. Based on the obtained data a tentative reaction mechanism was proposed. Kinetics of the degradation was also monitored for direct photolysis, as well as for solar degradation in the presence and in the absence of TiO_2.

(Malato S. et.al, 2002) The technical feasibility and performance of photo catalytic degradation of four water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) have been studied at pilot scale in two well-defined systems of special interest because natural-solar UV light can be used: heterogeneous Photocatalysis with titanium dioxide and homogeneous Photocatalysis by photo-Fenton. Experimental conditions allowed disappearance of pesticide and degree of mineralisation achieved in the two photo catalytic systems to be compared. In order to assure that the photo catalytic results are consistent, hydrolysis and photolysis tests have been performed with the four pesticides. Total disappearance of the parent compounds and 90% mineralisation have been attained with all pesticides tested, methomyl being the most difficult to be degraded with both treatments.

(Martin *et.al,* 2009) The influence of pesticide concentration, expressed as dissolved organic carbon (DOC), on combined solar photo-Fenton and biological oxidation treatment was studied using wastewater containing a mixture of five commercial pesticides, Vydate, Metomur, Couraze, Ditumur and Scala. Two initial DOC concentrations, 200 mg L^{-1} and 500 mg L^{-1} were assayed. Variation in biodegradability with photo catalytic treatment intensity was tested using *Pseudomonas putida*. Thus the mineralisation required for combining with biodegradation of intermediates by activated sludge was 33% and 55% at 200 mg L^{-1} and 500 mg L^{-1}, respectively. Bio treatment was carried out in a stirred tank in sequencing batch reactor (SBR) mode. As revealed by the biodegradation kinetics, intermediates generated at the higher pesticide concentration caused lower carbon removal rates in spite of the longer photo-Fenton treatment time applied. One strategy for treating water with high concentrations of pesticides and overcoming the low biodegradability of photo-Fenton intermediates is to mix it with a biodegradable carbon source before biological oxidation. This combination of photo-Fenton and acclimatized activated sludge in several SBR cycles led to complete biodegradation of a concentrated pesticide solution of 500 mg L^{-1} DOC in ~5 h with a carbon removal efficiency of 90%.

Ozone + Hydrogen peroxide (O_3 / H_2O_2)

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of OH radicals. ***(Pillard et.al, 1998)*** studied the elimination of atrazine in the filtered water. Result showed better degradation of the pesticides in water treated with ozone –hydrogen peroxide combination as compared to ozone alone. The optimum H_2O_2/O^3 mass ratio was from 0.35 to 0.45. ***(Duguet et.al., 1995)*** estimated the importance of H_2O_2 introduction point, and reported that the best performance was achieved when H_2O_2 was added after the oxidation of highly reactive substances with ozone alone. The implementation of a radical system makes oxidation of refractory molecules possible; it allows getting full advantages of selective molecules ozone reactions before converting the process to non-selective free radical attack.

0zone –UV radiation (O_3 / UV)

The use of O_3 / UV system brings about complete and fast mineralization of organic compounds present in the complex structure of pesticides with a short molecular chain 9 glyoxal ,glyoxylic acid and formic acid) can be achieved according to ***(Gurol & Vatistas 1987 and Takashi 1990)***

Fenton, photo-Fenton-like systems

(Keisuke, I. and Mohamed 2006) Pesticide pollution of surface water and groundwater has been recognized as a major problem in many countries because of the persistence of pollutants in aquatic environments and the consequent potential adverse health effects. Various hydrogen peroxide-based advanced oxidation processes, such as hydrogen peroxide/ultraviolet irradiation, Fenton, photo-Fenton, and electro-Fenton processes are likely key technologies for degrading and detoxifying these pollutants in water and wastewater. In this paper, the hydrogen peroxide-based advanced oxidation treatment of eight major groups of pesticides, namely aniline-based compounds, carbamates, chlorophenoxy compounds, organ chlorines, organophosphates, pyridine and pyrimidine derivatives, triazines, and substituted urea's, as well as that of several miscellaneous pesticides, is reviewed. The degree of pesticide degradation, reaction kinetics, identity and characteristics of degradation by-products and intermediates, and possible degradation pathways are covered and discussed.

CHAPTER-6

MATERIAL AND METHODS

This chapter describes the materials and methods adopted for carrying out the experimental work.

6.0 Materials

All the chemicals and other materials used in present study were purchased from reputed firms .The source has been mentioned wherever required.

6.0.1 Synthetic Sample

Chlorpyrifos pesticides with technical grade (99 % purity) were collected from S.D Agrochemicals limited Delhi, this industry is located at RG Complex II Sec 14, Rohini in New Delhi. The sample was given free of cost in plastic bottles and all the safety and precautions were guided with the help of pamphlets provided with it.

- Chemical name: O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate
- Empirical Formula $C_9H_{11}Cl_3NO_3PS$
- Trade names: Brodan, Detmol UA, Dowco 179, Dursban, Empire, Eradex, Lorsban, Paqeant, Piridane, Stipend
- Pesticide type: insecticide
- Class: organophosphate
- Mechanism of action: cholinesterase inhibitor

6.0.2 Chemical Structure

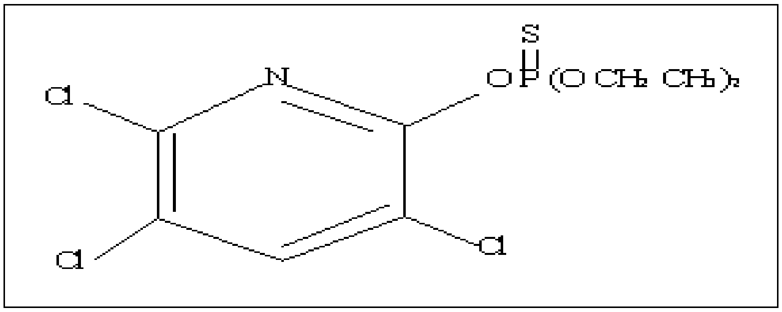


Fig : 6.1 Structure of Chlorpyrifos

6.0.3 Other Relevant Chemical and Physical Properties-

State: white, granular, crystalline solid

Melting point: 42 - 43.5°C

Vapour pressure: 1.87×10^{-5}mm Hg (at 25°C)
8.87×10^{-5}mm Hg (at 35°C)

Purity: 99.5%

Mol. Wt. 350.6

Solubility: Readily soluble in acetone, benzene chloroform, methanol and iso-octane; slightly soluble (0.4 ppm) in water.

When chlorpyrifos was exposed to UV light or to sunlight, it underwent hydrolysis in the presence of water to liberate 3, 5, 6-trichloro-2-pyridinol, which underwent further decomposition to diols and triols and ultimately cleavage of the ring to fragmentary products (Smith, 1968). The technical product is supplied in a variety of concentrations and formulations (emulsifiable concentrates, dusts, wettable powders and granules).

6.0.4 Background

Chlorpyrifos, a broad-spectrum organophosphate insecticide first registered for use in 1965, is one of the top five residential pesticides in use in the U.S. Registered uses include a wide variety of food crops, turf and ornamental, and greenhouse. An estimated 70% of urban usage is as a termiticide. The US EPA determined in June of 2000 that chlorpyrifos, common trade name Dursban, was sufficiently hazardous to human health as to warrant cancellation of nearly all the household-use products. Because of its extensive use, chlorpyrifos metabolites have been found in the urine 82% of adults sampled from the National Health and Nutrition Examination Survey, while the Minnesota Children's exposure Study found that 92% of 89 children evaluated had measurable urinary concentrations of 3,5,6-TCP, the primary urinary metabolite of chlorpyrifos.

6.0.5 Environmental Effects

- **Persistence:** Chlorpyrifos is moderately persistent in soils. The half-life is usually between 11 and 180 days but can range from 2 weeks to over a year, depending on soil type, climate and other conditions. In water at pH 7.0 and 25 degrees Celsius the half-life was 35-78 days in one study. Residues persist on plants from 10 to 14 days, and there is data that indicates that chlorpyrifos may accumulate in some crops.

- **Solubility:** slightly soluble in water at 2.0 mg / L.
- **Bioaccumulation**: Chlorpyrifos has the potential to bioaccumulation. It has been found to accumulate in the fat tissue of rats in one study, in the wing fat tissue of 800 hunter- killed northern bobwhite in a 1989 study, and in the tissues of fulvous whistling ducks collected in Florida. Bio concentration factors in fish studies have been documented at values of 58 to 5100.

6.1 Reagent and Chemical Used –

6.1.1 Photocatalyst TiO_2 – Titania was used as catalyst in whole experiment for enhancing the degradation rate of pesticide and this Titanium dioxide, also known as Titania is the naturally occurring oxide of titanium, chemical formula TiO_2.

Many studies have been published on the use of TiO_2 as a photo catalyst for the decomposition of organic compounds. TiO_2 is active under UV light

6.1.2 Oxidant H_2O_2 –In experiment Hydrogen peroxide was used as an oxidant; or H_2O_2, is a high-density liquid oxidizer with the unusual characteristic of being able to decompose exothermically into steam and oxygen. At room temperature, H_2O_2 has a very low vapour pressure and is relatively easy to handle in comparison to other rocket propellant liquid oxidizers, such as nitrogen ten-oxide (NTO), nitric acid, and liquid oxygen (LO_2). H_2O_2 is completely miscible with water and in general its physical properties are similar to that of water. Two notable differences between water and hydrogen peroxide are the much higher' density and the much lower vapour pressure of H_2O_2 in comparison with water.

6.1.3 COD Reagent Following chemicals were used for the COD estimation of chlorpyrifos pesticide and hence distilled water was used in whole experimental time for making reagents and for washing apparatus.'

1. Standard potassium dichromate solution, 0.25N: Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150°C for 2 h, in distilled water and dilute to 1000mL.

2. Sulphuric acid reagent: Add Ag_2SO_4, reagent or technical grade, crystals or powder, to conc. H_2SO_4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4. Let stand 1 to 2 days to dissolve. Mix.
3. Ferro in indicator solution: Dissolve 1.485 g 1, 10-phenanthroline monohydrate and 695mg $FeSO_4.7H_2O$ in distilled water and dilute to 100mL. This indicator solution may be purchased already prepared.
4. Standard ferrous ammonium sulfate (FAS) titrant, approximately 0.1N: Dissolve 40g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in 40 mL. conc. H_2SO_4, cool and dilute to 1000mL.
5. Potassium hydrogen phthalate (KHP) standard, $HOOCC_6H_4COOK$: Dry KHP to constant weight at 110°C. Dissolve 425mg in distilled water and dilute to 1000 m

6.2 Equipment and Instruments

6.2.1 pH Meter

The pH of the solution was adjusted with the help of 1N HCL and 1 N NAOH and measured using ELNICO, Indian LI 120-P^H

6.2.2 Filtration

After Photocatalysis treatments samples were filtered through injection filter (pore size 0.45).

6.2.3 Reactor

For the Photocatalysis process reactors used are made of borosil glass, which has a diameter 7.5 inches and is 2 inches in height with a capacity of approximately 1000 ml.

Fig.6.2 Inside View of UV-Chamber

6.2.4 COD Digester

COD digester was used for the digestion of the samples in the process of COD determination .Semi autoclave (EQUITRON) was also used for the same.

6.2.5 UV-Visible Spectrophotometer

The UV-visible spectrophotometer was used for the wavelength scan of raw pesticide sample and after the Photocatalysis treatment of the pesticides sample wavelength scan was taken with the help of spectrophotometer .The UV-Visible spectrophotometer was of HITACHI Company and model no (U-2800).

Fig.6.3. Spectrophotometer

6.3 Sample Preparation

Pesticides used in this experimental procedure was highly concentrated. Based on the survey in different regions of Punjab, the concentration i.e. 2 mg/L was used in the laboratory, i.e same concentration used by the farmers in the field. The sample was further diluted to get the COD values in the required range.

6.3.1 Using Shallow Pond Slurry Reactor

1. Stock solution of chlorpyrifos pesticide was prepared in distilled water for all the experiments.
2. The UV-tubes were turned on and all owed to warm-up for 30 minutes before the experiment was started.

3. Once the lamps warmed up, the lab jack (magnetic stirrer at its top) was raised or lowered.
4. Then 200 ml of pesticide sample was taken in the batch reactor, was added the optimum amount of catalyst.
5. This solution was kept under UV-lamp with continuous stirring using magnetic stirrer in the UV-chamber for the required period.
6. An aliquot of 5 ml was taken from the reactor at the regular interval of time with the help of syringe.
7. The catalyst was filtered from the sample by Millipore filter (0.45microm).These samples were analysed using UV-spectrophotometer as well as for COD estimation.
8. The pH of the final solution was taken.

All the experiments were carried out under the normal reaction conditions at intensity of 27 - 30 Wm^{-2}

6.3.2 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 waste water, 19809 (17 th Edition) .For all the samples appropriate dilutions were made so as to get COD within the range .Samples were digested in COD digester .

CHAPTER -7

RESULTS AND DISCUSSION

7.0 Pesticide Characteristics

Technical grade 99% pure chlorpyrifos pesticide was obtained from S.D Agrochemicals limited Delhi. The pesticide sample of technical grade was obtained and analyzed for its various parameters .The values of the various parameters are shown in **(T 7.1)** before treatment and Briefly, the experiment studied for photocatalytic treatment involves the following materials like different catalyst dose , different range of pH ,different H_2O_2 concentration and then after optimizing the different parameters the degration of the pesticides in the UV-Visible spectrophotometer at different time intervals were studied both by the COD reduction as well as by the absorption.

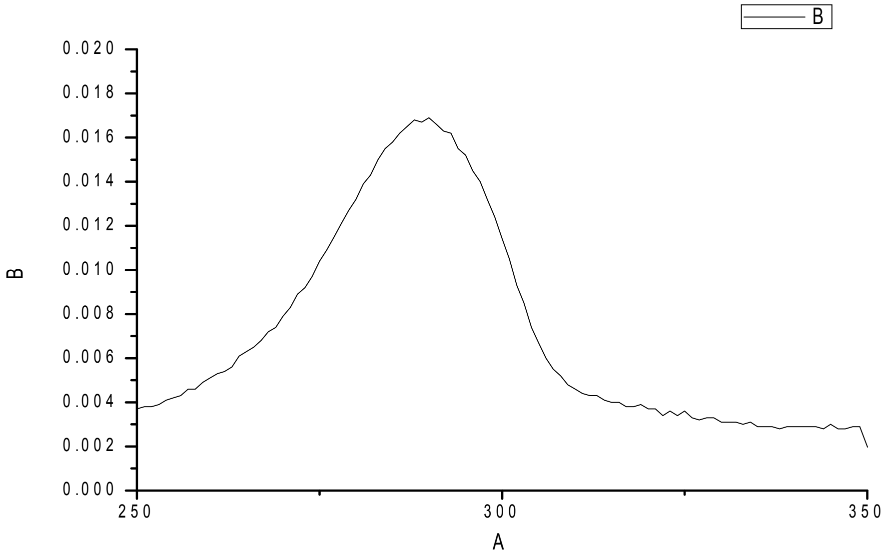
Parameters	**Values**
PH of chlorpyrifos	8.5 (basic)
COD of sample	12800 mg/l
Absorbance (max)	289 (nm)

T7.1 - Characteristics of the raw chlorpyrifos technical grade pesticides

Above listed parameters shows that the technical grade of the chlorpyrifos pesticide used in the fields by the farmers of Punjab is highly toxic. These organic chemicals are expensive and have many harmful effects, cause a number of pollution problems in the environment. In order to protect the environment , human health and adverse affect of this pesticide before releasing into the environment require proper treatment which satisfying the safe standards limits from environment point of view.

7.1 Absorption spectra of raw Pesticide sample

(Fig.7.1) Shows UV-Visible spectra of 2 ppm solution of technical grade chlorpyrifos pesticide showing sharp long peak at wavelength of 289 nm and absorbance 0.0169 which indicates that the pesticide is highly toxic and needs the effective degradation for the complete mineralization of the toxic compound to minimize the toxic effect.



A-Wavelength B-Absorbance

Fig 7.1 –Absorption spectra for the raw pesticide sample (2 ppm)

7.2 dark adsorption studies

Dark adsorption studies were carried out with the pesticide under study to correlate the results for adsorption and degradation under UV light. Chlorpyrifos pesticides organic matter was adsorbed on the surface of TiO_2. In this study, the pesticide of 200 ml was placed for many hours with the addition of the catalyst in the dark conditions without pH adjustments. The sample was tested after 10 hours to check the percentage in COD reduction and find 40 to 43% in COD reduction in pesticide sample i.e. is given in **(Fig 7.2)**.

The addition of the catalyst concentration in the dark showed a very little degradation. Continuous addition of catalyst TiO_2, monolayer formation on the catalyst surface occurs, after a period of time degradation rate became constant. After the monolayer formation reduction in COD values became constant As soon as the catalyst was added, pesticide from solution adsorbed on the surface, thus lead to decrease in COD values in the solution.
Thus results reveals from adsorption experiment confirmed that decrease in COD was due to adsorption of pesticide was confirmed. So for the complete degradation complex structure of

the technical grade pesticide into simpler non toxic compound addition alternative method should be used.

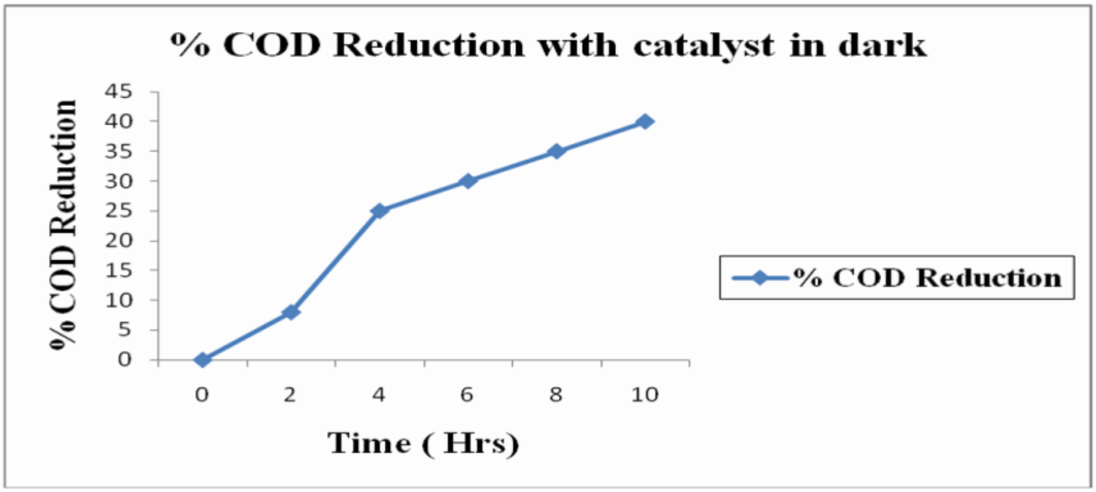


Fig 7.2 % COD reduction with catalyst in dark

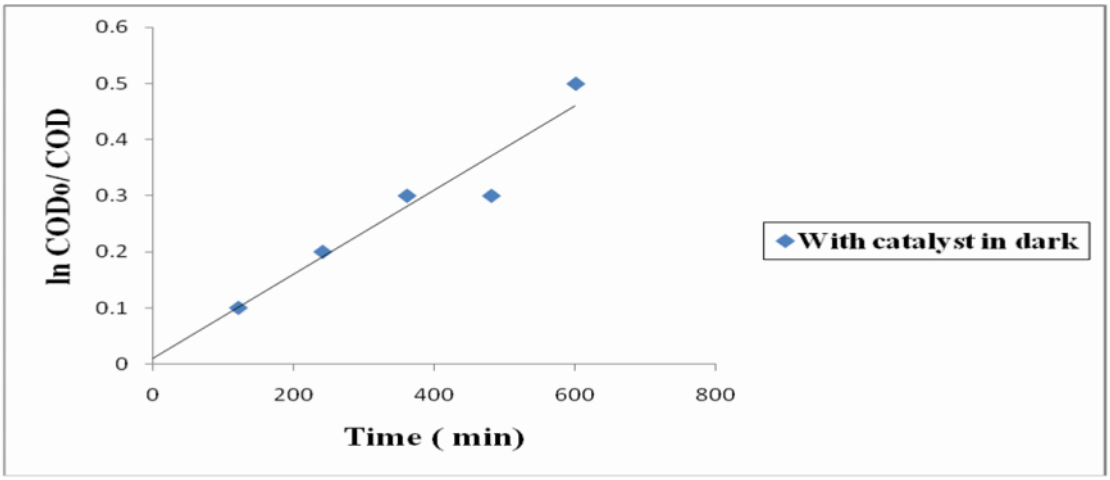


Fig 7.3 Linear transform of the kinetic curves of chlorpyrifos pesticide degradation with catalyst in dark

7.3 Photolytic Treatment

Photolysis treatment method for pesticides degradation is eco friendly method it completely mineralized organic compound into simpler ones. Reports confirmed about the direct photolytic degradation of some pesticides. To confirm, the pesticide in our study, the UV degradation of pesticide was done **Fig 7.4**. Minor degradation (8%) was observed, thus confirming that for the complete degradation of the pesticide advanced techniques would be best method for breaking complex structure of pesticide.

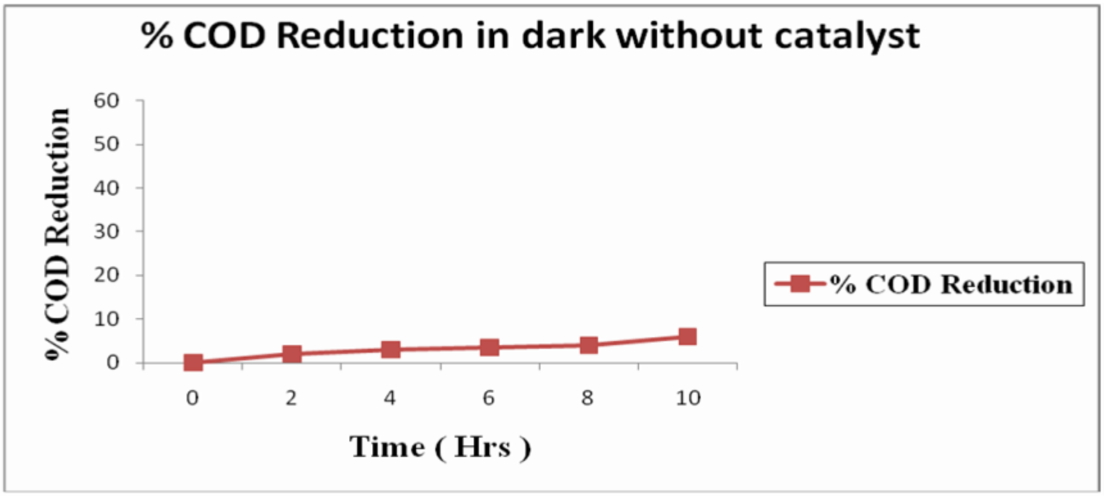


Fig 7.4 % COD reduction without catalyst in UV

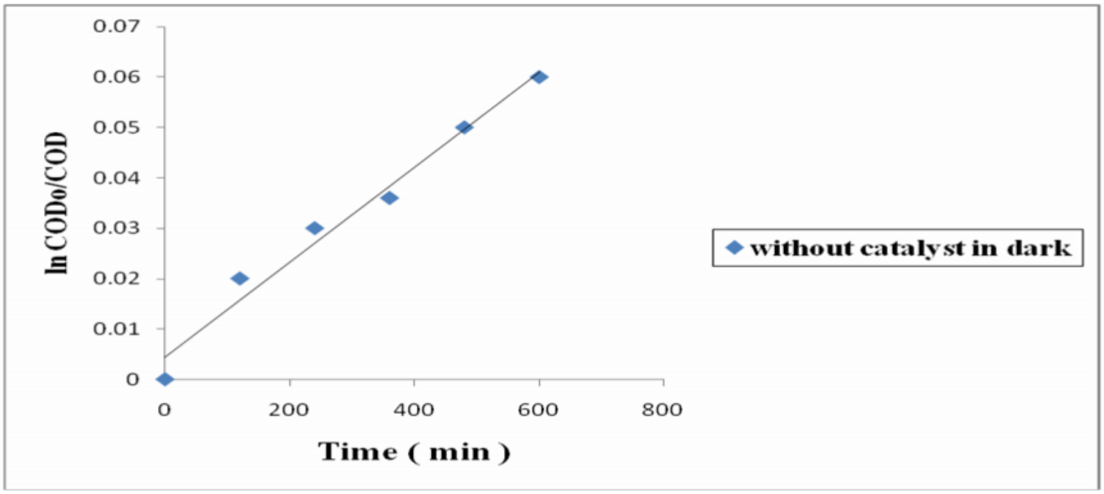


Fig 7.5 Linear transform of the kinetic curves of chlorpyrifos pesticide degradation without catalyst in dark

7.4 Photocatalytic treatment

After photolysis treatment method of chlorpyrifos pesticide, more advanced and efficient method is adapted in this study i.e. Photocatalytic treatment for degradation and minimization of toxic effect.

Following reaction scheme shows the stepwise photocatalysis using TiO_2.

$TiO_2 \longrightarrow TiO_2 (e^- + h^+)$

$h^{+} + RX_{ad} \longrightarrow RX_{ad}^{\cdot +}$

$h^{+} + H_2O_{ad} \longrightarrow HO_{ad}^{\cdot} + H^{+}$

$h^{+} + OH_{ad} \longrightarrow HO_{ad}^{\cdot}$

$e^{-} + O_2 \longrightarrow O_2^{\cdot -}$

$e^{-} + H_2O_2 \longrightarrow OH- + HO.$

Where R indicates the solute organic molecule and the subscript 'ad' indicates the adsorbed species on catalyst surface. Since the photocatalysis is a radical reaction the completion of the reaction depends on a number of parameters like

1. Intensity of irradiation
2. Catalyst loading – type and amount of catalyst
3. Operating pH
4 Oxidant additions

So depending upon these above listed factors, optimized reaction conditions were calculated and used throughout the process

Several research paper results indicated that the destruction rates of photocatalytic oxidation of various organic contaminants over illuminated TiO_2 fitted the Langmuir–Hinshelwood (L–H) kinetics model

$$r = dC/dt = kKC/1+KC$$

where *r* is the oxidation rate of the reactant (mg/l min), *C* the concentration of the reactant (mg/l), *t* the illumination time, *k* the reaction rate constant (mg/l min), and *K* the adsorption coefficient of the reactant (l/mg).

When the chemical concentration C_0 is a millimolar solution (C_0 small) the equation can be simplified to a apparent first-order equation

$$ln\ C_0/C = kKt = k_{app}t \text{ or } C_t = C_0\ e^{-k_{app}t}$$

A plot of ln C_0/C versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k_{app}. Generally first-order kinetics are appropriate for the entire concentration range of ppb or few ppm.

7.4.1 Radiation conditions during experiment

Intensity of irradiation affects significantly in reaction initiation step and at higher intensities, the rate is found to be more. During experiment specifically kept intensity ranges from 25-28 W/m^2 is just to match intensity of UV radiations that we are getting from sunlight so that the industrial applications could be looked into.

7.4.2 Catalyst concentration

In our experimental study we used titanium dioxide as a catalyst for the degradation of pesticide because of its efficiency of mineralization of organic compounds. The concentration of catalyst (TiO_2) was varied from 0.1% to 1.0% in 200 ml sample, for studying the pesticide degradation rate. It was observed that degradation rate of pesticide increases with increased catalyst concentration and becomes constant above a certain level as shown in (**Fig 7.6)** and after one particular optimize dose the degradation rate of the pesticide starts to decrease.

The reason for this decrease in degradation is due to the decrease in surface area of catalyst due to aggregation of TiO_2. Catalyst 0.4% was found to be the optimum dose at which the highest COD reduction was observed and after this catalytic dose COD reduction, goes on decreasing as shown in the given figure. An optimum of catalyst concentration has to be taken when the decrease in COD level are to be within acceptable limits.

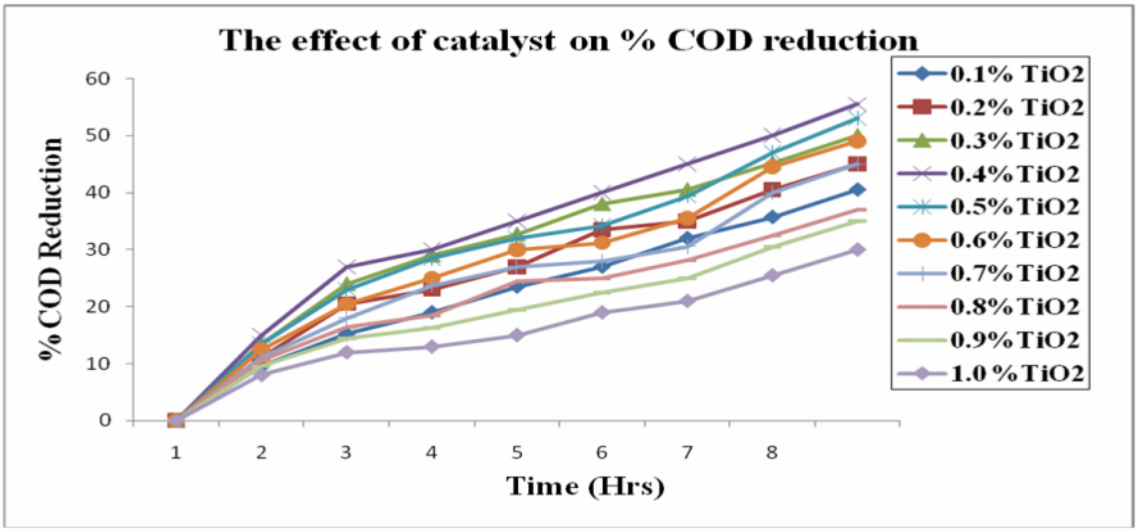


Fig 7.6 Effect of catalyst concentration on the COD reduction

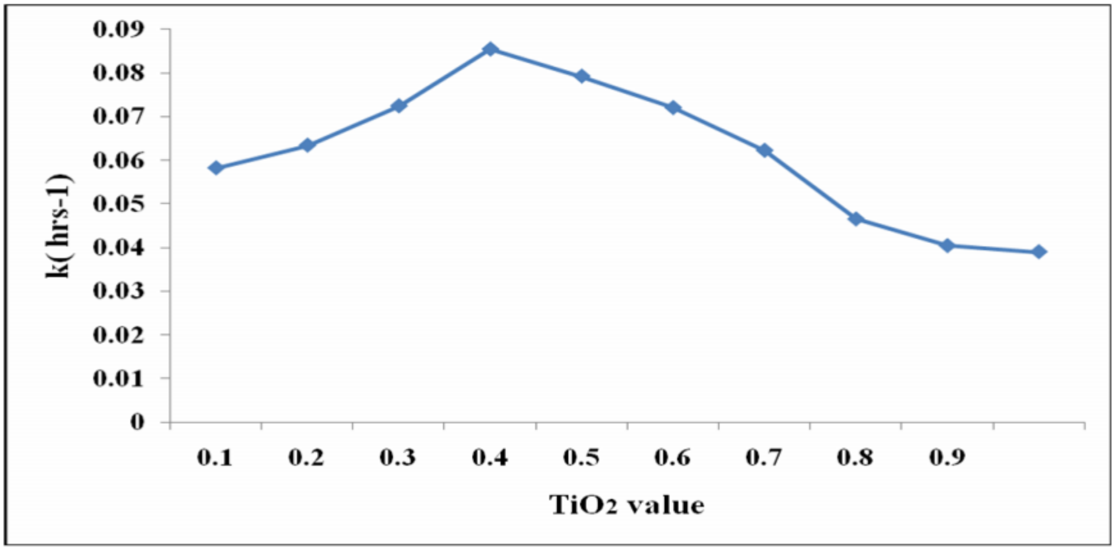


Fig 7.7 Effect of TiO_2 rate constant k

7.4.3 Effect of operating pH

Results of the photocatalytic degradation of chlorpyrifos solution at different initial pH values are presented in Fig 7.8. The pH plays an important role in the complete mineralization of pesticides, so a photochemical reaction experiments that were carried from different pH values i.e. 3.5 to 8.5. It also indicates that high pH values increased the initial rate of photocatalytic reactions and at pH 6.5 with catalysts shows maximum degradation about 90 % by calculating the COD value after treatment ,was observed as shown in the **(Fig 7.8),** after that decrease in the degradation rate starts. It is coated in many literatures that varying the pH of the reaction system varies the surface charge of TiO_2.

In our experiments, maximum conversion of the pesticide was obtained at 6.5 pH.Optimum pH should be at 6.5 because maximum degradation was achieved at this pH, beyond this pH the degradation rate of pesticide decreased.

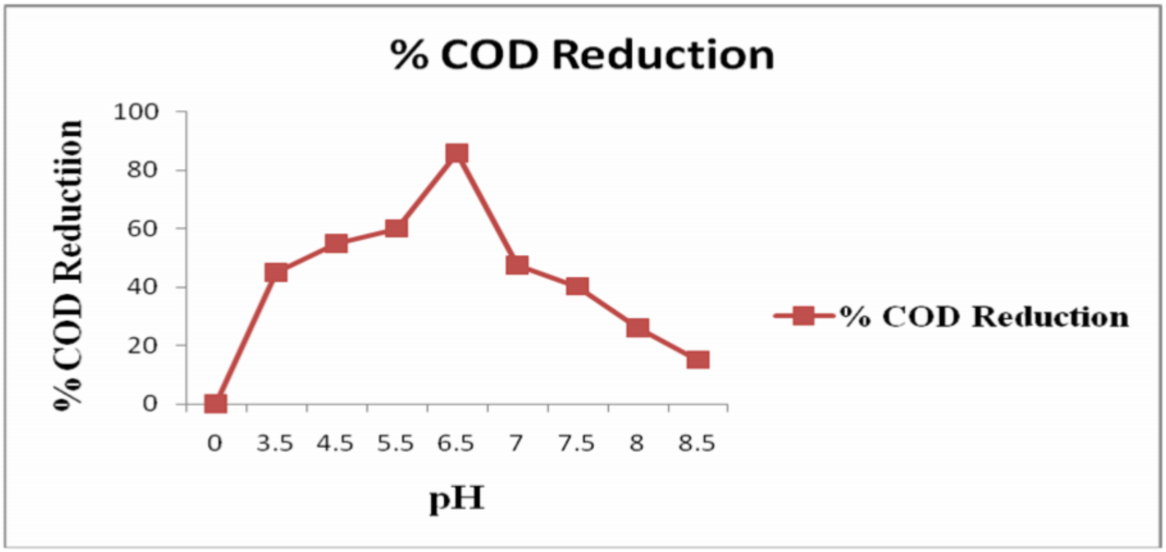


Fig 7.8 Effect of pH on the % degradation of the pesticide solution

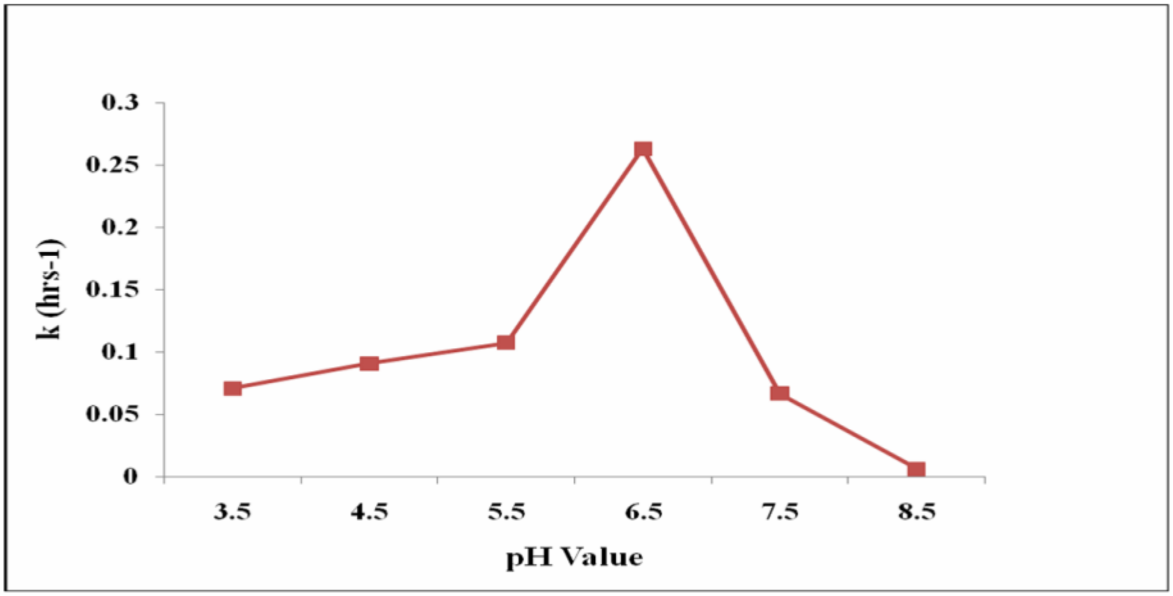


Fig 7.9 Effect of pH rate constant k

7.4.4 Effect of Oxidant addition

According to many researchers hydrogen peroxide is a well-established and significant commercial chemical, for treating waste water and other organic compounds. Thus due to high oxygen supplying property of Hydrogen peroxide was used as additional oxidant in our experiment for enhancing the photo catalytic activity by reducing the rate of recombination between the holes and electrons in the activated titanium dioxide particles.

The experiments conducted by varying the hydrogen peroxide concentration from 0.5 to 3.5 ml per 200 ml of the pesticide sample. The best results were obtained when oxidant addition came out to be 2 ml/200ml of pesticide sample and have been taken as the optimum amount required for maximum effective degradation of toxic pollutants. **(Fig 7.10)** shown below shows that 2 ml is the optimum dose of the oxidant H_2O_2 at which maximum pesticide degradation was observed.

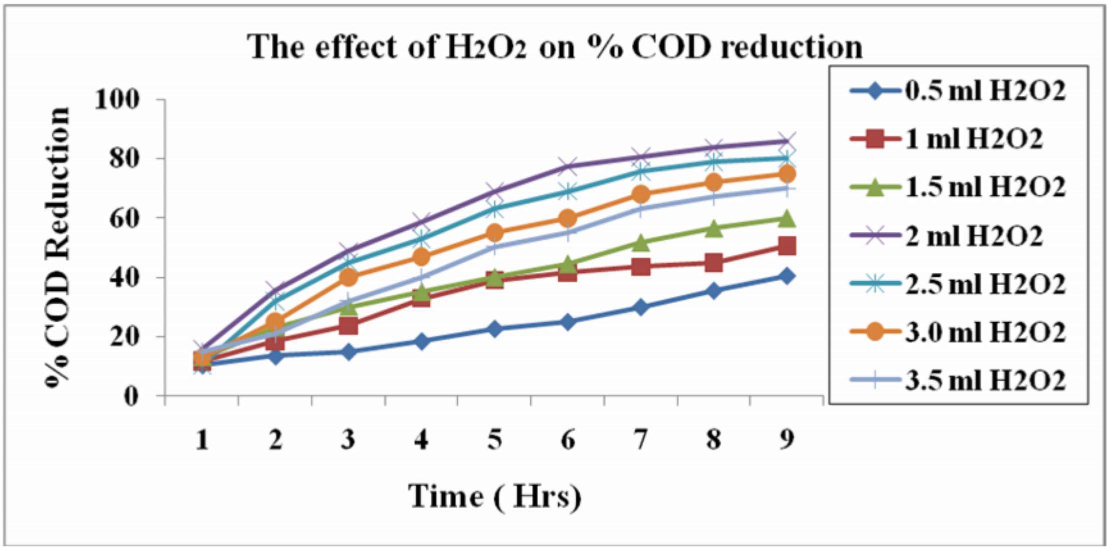


Fig 7.10 Effect of H_2O_2 on the % degradation of the pesticide solution

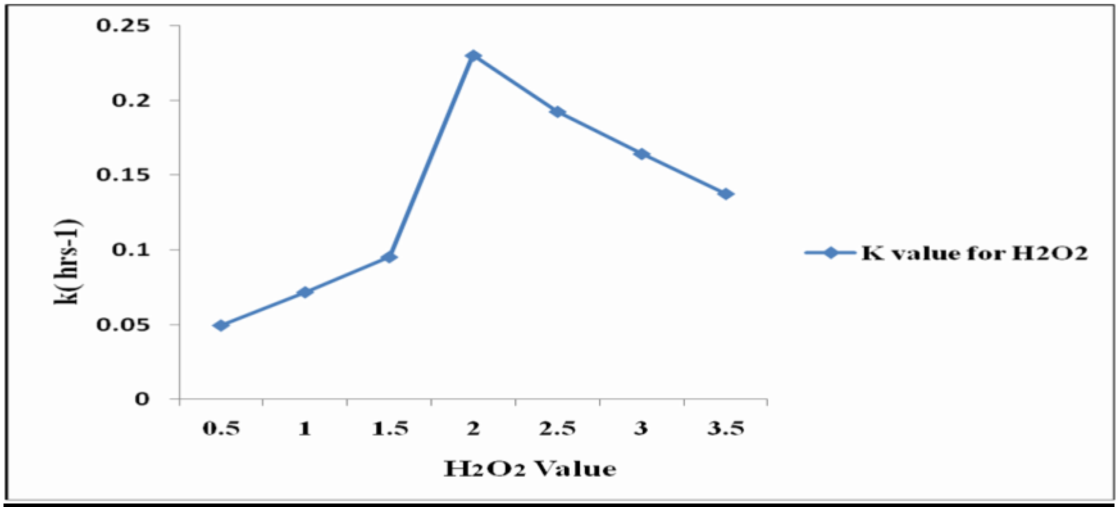


Fig 7.11 Effect of initial H_2O_2 on rate constant

7.5 Effect of Sonication in degradation

The optimized result was compared with when TiO_2 was added after sonication of one hour duration. Sonication helps in uniform dispersion of catalyst particles in the suspension thus helps in creating more surface area for photocatalytic reactions. So when there is more surface area there is more photocatalytic reaction and more percentage of degradation rates.

It is cited in many literatures that for achieving uniform dispersion this TiO_2 slurry was sonicated by ultrasonic bath with ultrasonic frequency of 16 -20 KHz.

This sonicated catalyst was then added to the 200 ml sample by optimizing the conditions with UV source i.e. 0.4% TiO_2, 6.5 pH, 2 ml H_2O_2 addition, the degradation studies were carried out, average intensity was nearly 27-30 W/m^2.

It was observed **(Fig 7.12)** that the degradation of the pesticide was maximum when sample was treated with sonicated catalyst slurry i.e. 93% degradation during treatment of sample with sonicated catalyst slurry under UV-light for same time and under same optimized conditions. The sample without sonicated catalyst was found to be less degraded i.e. 71 % in same optimized conditions.

Hence it is clear from this study; UV-light with sonicated catalyst slurry makes the degradation rate so much fast than the non sonicated catalyst slurry, so it would be the best advanced technique for treating the organic waste like pesticide waste etc along with optimized parameters.

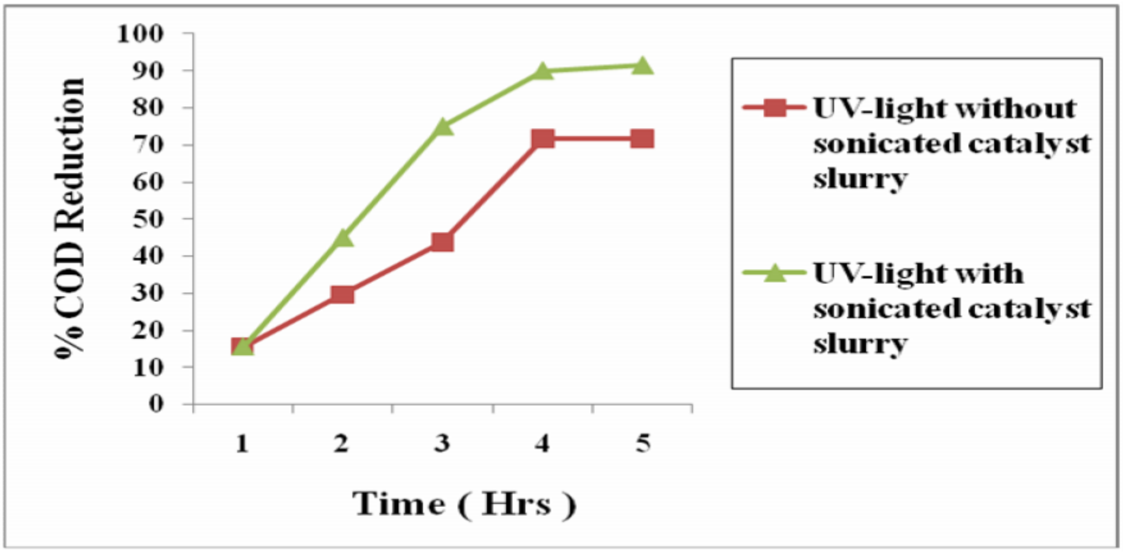


Fig 7.12 % photo degradation efficiency Vs. Time

7.6 Comparison studies of degradation of pesticide under UV- light and Solar radiations

Results obtained from the degradation studies of pesticide using artificial UV light with sonicated catalyst from sonicated batch reactor was compared with treatment under solar radiation. After optimizing the conditions with UV source i.e. 0.4% TiO_2, 6.5 pH, 2 ml H_2O_2 addition, the degradation studies were carried out under natural solar conditions. The average intensity was nearly 27-30 W/m^2, same as we kept during artificial UV treatment, before using catalyst that catalyst treated under ultrasonic frequency in sonicator for 1 hour then this catalyst is added in sample and hence degraded in UV-light for 5 hours and

Hence results showed in **(Fig 7.13)** sample degraded by solar light i.e. 87 % degradation, with optimized parameters is more than sample degraded under UV- light with catalyst is 71 %. So treatment of pesticide sample under solar light with optimized parameters is efficient technique than the sample treated in UV-light.

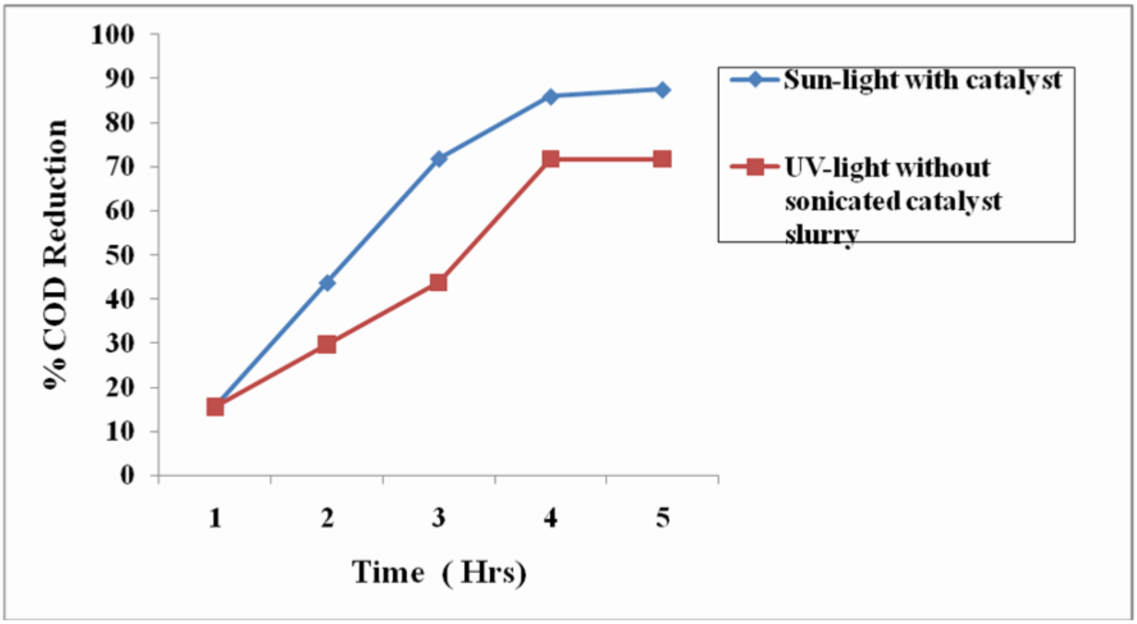


Fig 7.13 % photo degradation efficiency Vs Time

7.7 Absorption spectra after photo catalytic treatment

(Fig 7.14) given below is a set of UV-Visible spectra showing the complete disappearance of 99% technical grade chlorpyrifos pesticide from water when passed through photocatalytic treatment .

Complete removal of the pesticides from water was confirmed by UV-Visible spectroscopy after photocatalytic treatment given for 2 ppm sample with optimized conditions i.e. 2ml H_2O_2, 0.4% TiO_2 catalyst and 6.5pH for 10 hours in UV-reactor. The toxic and harmful compounds mineralized into non toxic compound. As in this spectra no peak was observed in the UV as well as visible region i.e. the peak observed in the raw sample was completely disappeared after treating the sample with optimized conditions in the UV-reactor. The method offers a convenient and cost-effective means of removing pesticides from water.

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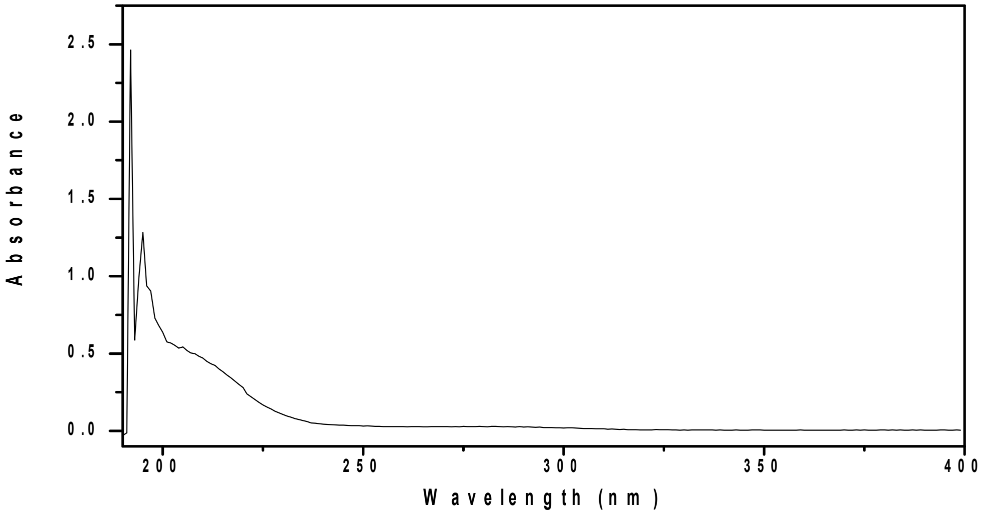

Fig 7.14- Absorption spectra for pesticide after photo catalytic treatment

7.8 Catalyst recycling

TiO_2 was reused in photocatalysis for treatment of Pesticide waste water, TiO_2-catalyst suspensions work efficiently in photocatalysis for wastewater treatment. Nevertheless, once photocatalysis is complete, separation of the catalyst from solution becomes the main problem; the catalyst was filtered by using wattmann filter paper no.22 catalyst. Reuse of the catalyst after it had settled to the bottom and clear water had been removed and catalyst was activated at 105 ^{0}C. Photocatalytic efficiency worsens with successive runs when catalyst and water are reused without separation, whereas, when TiO_2 is separated, the Photocatalyst is not deactivated.

There are two major cause behind the reduction in the efficiently, catalyst fouling and loss of catalyst during filtration, during experiment for catalyst recycling, TiO_2 recycled for at least five times as shown in **(Fig 7.15)** but with the reduction in the degradation efficiency. The catalyst lifetime is an important parameter for industrial application of photo catalyst and also to reduce the cost of the catalyst significantly.

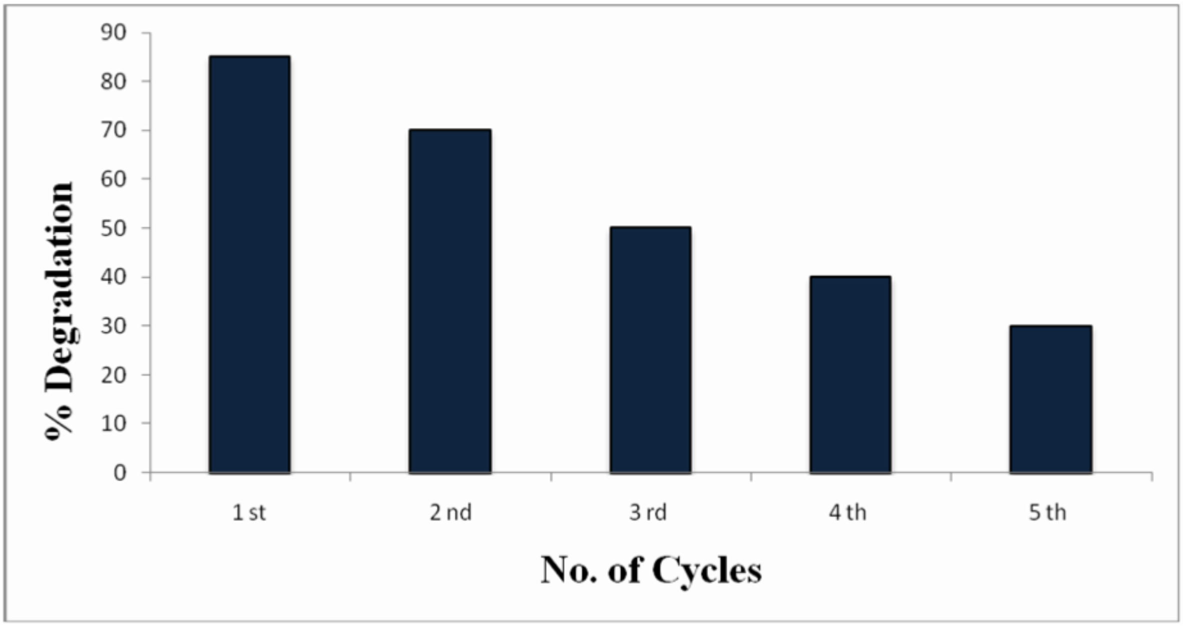

Fig 7.15 Catalyst (TiO_2) recycling

CHAPTER-8

CONCLUSION AND RECOMMENDATION

Conclusions

In advanced oxidation process, Photocatalysis process can be efficiently degrade the pesticides using artificial UV- light or sunlight radiation sources. The observations, clearly demonstrated the important of cooling optimum degradation parameters to obtain high degradation rates which is most essential for practical applications of Photocatalysis oxidation processes. In this work, the Photocatalysis oxidation of chlorpyrifos pesticide has been studied using TiO_2 as a photo catalyst and H_2O_2 oxidant. Studies reveal that photo catalytic oxidation of the pesticide in a shallow pond reactor can be efficiently done. The optimum conditions for the photo degradation of pesticides are 0.4% catalyst concentration, 2 ml H_2O_2 and 6.5 PH.

Results can be implemented with certain modifications at large level, to effectively remove pesticides from water or waste water which are not removed by conventional treatment. Large shallow pond reactors can be made and implemented in conventional treatment to treat water containing pesticides.

But, prior to developing a full scale pond reactor tests or experiments should be conducted with a prototype system to calculate the typical values of the rate constant, because Photocatalysic degradation process or rates are highly dependent on the molecular structure of the solute.

Recommendations

Much work is needed to develop, more accurate method for modelling the kinetics of water and waste water containing pesticides. Advanced oxidation processes for water and waste water applications either using artificial UV- light or solar light will advantageously complete in the market. In overcoming one of the major challenges i.e. a treatment cost and advanced oxidation process there is a need of the future research that must lead to the reduction of the treatment cost. Future research must also investigate the effectiveness of these technologies in the combination with other cost effective treatments such as biological treatment of bio-recalcitrant compounds, where each technology by itself may not be sufficiently effective for the degradation of toxic compounds.

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