ADVANCED OXIDATION PROCESSES FOR THE DEGRADATION OF PESTICIDES

A Thesis Submitted

In partial fulfillment for the award for the

Degree of Master of Technology in

Environmental Science and Technology

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Certificate

I hereby certify that the work that is being presented in the thesis entitled “Advanced Oxidation Processes (AOP’s) For The Degradation Of Pesticides”, submitted by Ms Monika Sheoran in partial fulfillment of the requirements for the award of the degree of Master of Technology submitted in Department of Biotechnology and Environmental Sciences, Thapar University, Patiala is an authentic record of my own work carried under the supervision of Er. Anoop Verma. The report has not 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

Photocatalysis process, as an environmental application is a relatively novel subject with tremendous potential in the near future. The basics of heterogeneous photocatalysis, mainly depends on TiO_2 and the application of photocatalytic processes to water purification and treatment. Heterogeneous photocatalysis is rapidly expanding Technology for water and air. Hazardous organic wastes from industrial, military, and commercial operations represent one of the greatest challenges to environmental engineers. The use of high energy oxidants such as ozone and H_2O_2 and/or photons those are able to generate highly reactive intermediates $^{\cdot}OH$ radicals. During the last few years, there has been a plethora of research and development in the area of solar photocatalysis (TiO_2 and photo-Fenton). This overview, of the most recent papers on the use of sunlight to produce the ·OH, comments on those most relevant to the development of the technology and summarizes most of the recent research related to the degradation of water contaminants, and pesticide degradation and how solar photocatalysis (coupled with biotreatment) could significantly contribute to the treatment of very persistent toxic compounds. Photodegradation of different herbicides occurred in both aqueous systems; however the presence of TiO_2 clearly accelerated the degradation of the three herbicides in comparison with direct photolysis. In the project the technical grade pesticide Malathion degradation was studied which is collected from Dhanuka group of pesticide industries (New Delhi).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 Malathion 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 technical grade pesticide, Malathion degradation was observed nearly 80% by measuring COD reduction and complete adsorption on the TiO_2 photocatalyst was observed during the experimental work in the lab.

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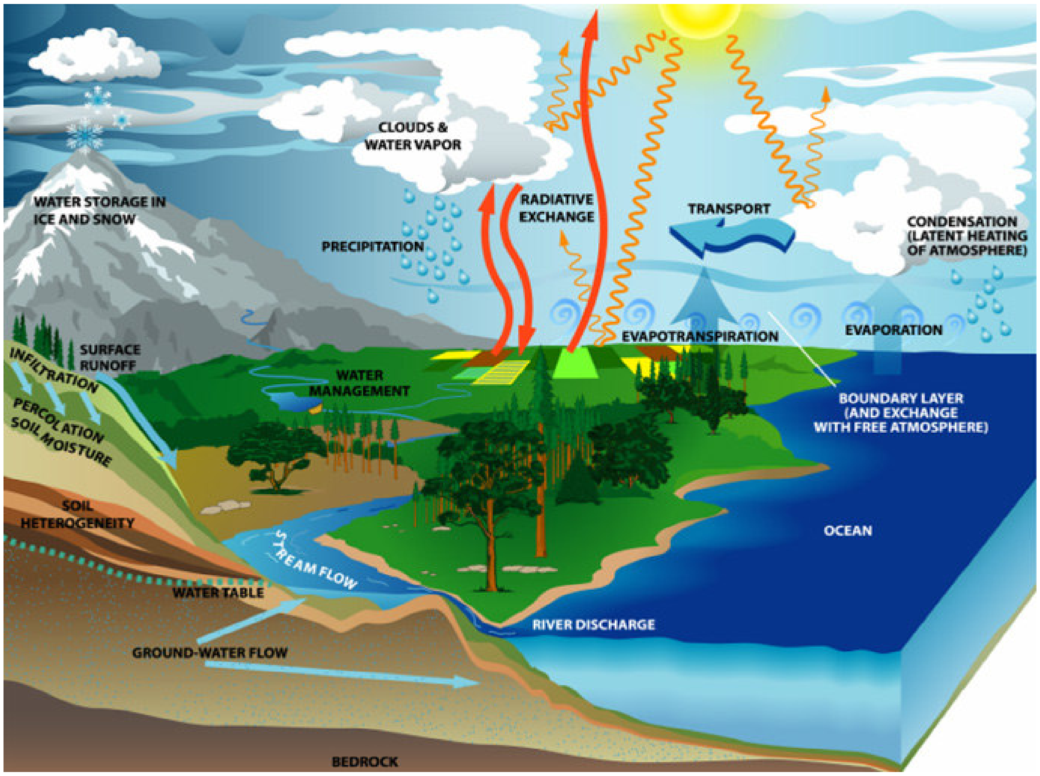
INTRODUCTION

1.0 Environmental Pollution

The atmosphere is a paper-thin layer of gas (representing 1 percent of the mass of Earth) that protects the planet from damaging cosmic and ultraviolet radiation, contains life-giving oxygen, and allows the efficient cooling of the planet. Environmental pollution is the release of chemical waste that causes detrimental effects on the environment. Environmental pollution is often divided into pollution of water supplies, the atmosphere, and the soil or pollution can also be defined as an undesirable change in physical, chemical, biological characteristics of air, water and land that may or will adversely affect human life, industrial progress, living conditions and cultural assets. (Odum, 1971)

1.1 Water Pollution

Fresh, clean, and drinkable water is a necessary but limited resource on the planet. Industrial, agricultural and domestic wastes can contribute to the pollution of this valuable resource and water pollutants can damage human and animal health. Three important classes of water pollutants are heavy metals, inorganic pollutants and organic pollutants. Heavy metals include transition metals such as cadmium, mercury, and lead, all of which can contribute to brain damage. Inorganic pollutants like hydrochloric acid, sodium chloride, and sodium carbonate change the acidity, salinity, or alkalinity of the water, making it undrinkable or unsuitable for the support of animal and plant life. These effects can result in dire consequences for higher mammals such as humans. A list of organic pollutants includes pesticides such as chlorpyrifos and paraquat, and their byproducts, such as dioxin. All of these substances are highly lethal to animals, and many can be readily absorbed through the skin. **F 1.1** shows how water movement takes place from atmosphere to surface.



F 1.1 - Showing the hydrological cycle.

Water also will flow to the lowest point allowed by the geologic and soil structures present in the environment.

1.2 The problematic of water pollution

One of the characteristics that best defines today's society in what is understood by the developed countries is the production of waste products. There is practically no human activity that doesn't produce waste products and in addition, there is a direct relationship between the standard of living in a society or country and the amount of waste products produced. Approximately 23% of the world's population lives in developed countries consume 78% of the resources and produce 82% of the waste products (Blanco and Malato, 1996). In addition, it has to be pointed out that the volume of residual waste increases in an exceptional way with regards to a country's level of industrialization. At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide, and it is estimated that 1000 new chemical substances are added to the list each year. The permitted levels have been vastly exceeded causing serious environmental concerns. The main problem stems from industry and agriculture, pesticides, despite the fact that the population also plays an important role in the environment contamination.

Dyes, phenols, pesticides, detergents and other chemical products are disposed of directly in to the environment, without being treated, controlled or uncontrolled and without an effective treatment strategy.

In this general context, is very clear that the strategy to continue the search for solutions to this problem that every day presents a sensitive growth, mainly in the developing countries, will be guided to two fundamental aspects:

- The development of appropriate methods for contaminated drinking, ground and surface waters.
- The development of appropriate methods for wastewaters containing toxic or non-biodegradable compounds.

Non- biodegradable are persistent materials in the case of not receiving a specific treatment necessary for their destruction or inertness, they can affect various sectors of the environment. From this, a series of very diverse and irreversible damage can result, ranging from the deterioration or disappearance of a determined environment to changes in the health of those individuals who live in that environment. A large part of this type of residual waste is generated in an aqueous solution and, owing to its non-biodegradable nature, the biological treatment procedures (the most commonly used) are not effective, and unless there is an additional specific treatment, they end up being dumped in the environment. The presence of this type of pollutant in an aqueous dissolution is especially problematic as the residual waste cannot be stored indefinitely (as is the case with some solid waste) and it has the peculiarity that a small volume of water is able to contaminate much greater volumes of water.

The situation by the lack, or insufficiency, of adequate water treatment systems capable of diminishing the concentration of toxic substances that represent a chronic chemical risk. It can be said that badly treated wastewaters lead inevitably to a deterioration of water sources quality and consequently, of drinking water. It must be pointed out that a wide spectrum of compounds can transform themselves into potentially dangerous substances during the drinking water treatment process, particularly by chlorination, as is the precursor compounds of the formation of chlorocarbons (Marhaba and Washington, 1998).

Dangerous and toxic waste is defined as "those solid, semi-solid, and liquid materials, as well as those gaseous materials in recipients, which are the result of a process of production, transformation, use or consumption which are destined to be abandoned and whose composition contains some of the substances or materials that figure in the successive revisions by the EU committee, in such quantities or concentrations that represent a health to humans, natural resources and the environment and that need a treatment process or special elimination". The European Union made out a list of dangerous compounds, considered as contaminants, to which constantly new substances are added (black list of the E.U., **See T 1.1)**

GROUP	**INCLUDED SUBSTANCES**
Chloride hydrocarbons	Aldrin,dieldrin,chlorobenzene, dichlorobenzene,endosulphane,endrin, hexachloroethane, trichlorobenzene.
Pesticides	Cyanidechloride,DDT,dementon,dimethoate, disulfoton,monolinuron,omethoate, propanyl,pirazone,simacine,raxil (fungicide).
Chlorophenol	Monochlorophenol, 2-, 4-dichlorophenol, 2-amino-4-chlorophenol, trichlorophenol.
Polycyclic aromatic hydrocarbons	Anthracene, biphenyl, PAHs.
Inorganic substances	Arsenic and its compounds, cadmium and its compounds, mercury and its compounds.
Solvents	Benzene,chloroform,dichloromethane, dichloroethylene,dichloropropane, trichloroethylene.

T 1.1 - Showing black listed compounds of the E.U.

1.3 Pesticide pollution

The problem of the pesticide pollution is increasing day by day due to its maximum use in the agricultural field and also pesticide contaminated water if taken above the permissible limits it may lead to the serious health problems such as vomiting, nausea, diarrhea, hypertension and many others health related problems.

Pesticide is a general term for substances, which are used to poison pests (weeds, insects, molds, rodents etc.). The pesticides most acutely dangerous to humans are insecticides and rodenticides. Synthetic pesticides have been popular with farmers, because of their widespread availability, simplicity in application, efficacy and economic returns. But they also have huge environmental costs. After India's Green Revolution started, the consumption of pesticides in India has increased several hundred folds, from 154 MT in 1954 to 88,000 MT in 2000-2001.

According to industry estimates, the pesticide use has high growth potential in India, as the use of agricultural pesticides is markedly low at 0.54 kg /ha as against 3.7 kg/ha in USA and 2.7 kg/ha in Europe. Notwithstanding the fact that Overall consumption of pesticides in India as a whole is low than that used in the developed countries of the world, there is still a widespread contamination of water, soil and air with pesticide residues.

Table **(T 1.2)** showing the **47349** reported cases of pesticide poisoning in India from 1992-1996. In India, among different states maximum consumption of pesticides-1999-2000 was in Uttar Pradesh (7459 MT) followed by Punjab (6972 MT), Haryana (5025 MT), Andhra Pradesh (4054 MT), Gujarat (3646 MT). Leading pesticides used in India include monocrotrophos (10700 MT- highest consumed), acephate (6400MT), endosulfan (5600 MT) and chlorpyrifos (5000 MT - fourth highest consumed), Malathion (Source: Pesticide Information, Volume XXVIII, No. 3, October- December 2002).

Year	1992		1993		1994		1995		1996		Total	
	Cases	%	Cases	%	Cases	%	Cases	%	Cases	%	Cases	%
Insecticide	61 497	87.1	45 231	86.5	37 446	87.5	41 404	85.6	27 999	84.2	213 577	86.3
Fungicide	766	1.1	681	1.3	446	1.0	403	0.8	1401	1.2	2697	1.1
Rodenticide	1497	2.1	1407	2.7	1141	2.7	1389	2.9	1079	3.2	6513	2.6
Herbicide	773	1.1	607	0.9	417	1.0	531	1.1	502	1.5	2830	1.2
Mixed	1170	1.6	452	0.9	486	1.1	1120	2.3	468	1.4	3696	1.5
Others	4915	7.0	3909	7.5	2876	6.7	3530	7.3	2806	8.4	18 304	7.3
Total	70 168	100	52 287	100	42 812	100	48 377	100	33 255	100	247 349	100

T 1.2 - Showing the reported cases of pesticide poisoning (1992-1996).

1.4 Major sources of pollution

- Point sources of pollution.
- Non-point sources of pollution.

Point-source pollutants in surface water and groundwater are usually found in a plume that has the highest concentrations of the pollutant nearest the source (such as the end of a pipe or an underground injection system) and diminishing concentrations farther away from the source. Point sources of pollution from agriculture may include animal feeding operations, animal waste treatment lagoons, or storage, handling, mixing, and cleaning areas for pesticides, fertilizers, and petroleum. Municipal point sources might include wastewater treatment plants, landfills, utility stations, motor pools, and fleet maintenance facilities. The major point sources of pesticide pollution are waste-waters from agricultural industries, pesticide formulating or manufacturing plants. Wastewater from these sources may have pesticide contamination levels as high as 500 mg/l.

Nonpoint-source pollution occurs as water moves across the land or through the ground and picks up natural and human-made pollutants, which can then be deposited in lakes, rivers, wetlands, coastal waters, and even groundwater. The water that carries nonpoint-source pollution may originate from natural processes such as rainfall or snowmelt, or from human activities such as crop irrigation or lawn maintenance.

Different pesticides used in the fields are as follows:

- Atrazine
- Alachor
- Aldicarb
- Carbofuran
- 2,4-D
- Diquat
- Endothall
- Glyphosate
- Lindane
- Malathion
- Endosulfon
- Methoxychlor

Out of all these pesticides, malathion was selected for our study purpose.

1.5 Malathion

The work was done on the technical grade of the malathion obtained from the Dhanuka group of the pesticide industries, New Delhi. The degradation of the technical grade malathion having purity greater than 90% was observed during the experimental work. Some of the brief introduction of the malathion is given as below:

1) Malathion is an insecticide that was registered for use in the United States in 1956.
2) Malathion belongs to a class of insecticides know as organophosphates (Ops).
3) Malathion is yellow to brown liquid with a skunk-or garlic like odor. It dissolves slightly in water and doesn't readily evaporate in the air.. it may damage metal and some form of plastic and rubber.
4) Malathion products are used to control a variety of insects outdoors and are sold in the form of dusts, liquids aerosols and wettable powders.

1.5.1 How does Malathion works?

- Malathion kills insects by interrupting the nervous system. It does this by inhibiting an enzyme called cholinesterase.

- Malathion affects the nervous system of insects and humans. Insects are more susceptible to this than mammals.

1.5.2 Malathion Exposure

Malathion exposure mainly takes place by a number of ways three main ways of malathion exposure are as follows:

1. **Ingestion**
2. **Inhalation (lung)**
3. **Skin (dermal)**

Like Accidental ingestion, Lawn and garden use, Insect control, Food supply, Water supply etc.

F 1.2 - Showing malathion harmful effect on wildlife.

1.6 Objectives

The main objectives of the proposed study are:

- Survey and selection of pesticide, used mostly in Haryana region.

- Heterogeneous photocatalytic treatment of the pesticide, using TiO_2 as one of the photocatalyst and process optimization by varying operating conditions.

1.7 Approach

1. Survey and selection will be done in the Haryana region; by continuous visiting in different fields. Thus the most commonly used pesticide/herbicide will be selected.

2. The Selected pesticide would be treated using Advanced Oxidation Process i.e. heterogeneous photo catalytic treatment. Degradation would be studied by continuously measuring the COD.

3. Then degradation conditions would be optimized by varying the catalyst concentration, pH and addition of suitable oxidant.

4. Catalyst recyclability would be checked as it could be an important step towards the economical applications.

CHAPTER 2
PESTICIDES AND THEIR SCENARIO

2.0 History of pesticides and their scenario in India

The use of chemical pesticides and fertilizers in Indian agriculture has seen a sharp increase in recent years. In some areas, such as Haryana, Punjab and west Uttar Pradesh, it has reached alarming levels. The heavy use of these chemicals has already caused grave damage to health, ecosystems and ground water. It is therefore increasingly urgent that environmentally friendly methods of improving soil fertility and pests and disease control are used.

2.0.1 Pesticides

The use of pesticides in agriculture contributes to environmental pollution. Pesticides are used to control the growth of insects, weeds, and fungi, which compete with humans in the consumption of crops. This use not only increases crop yields and decreases grocery prices, but also controls diseases such as malaria and encephalitis. However, the spraying of crops and the water runoff from irrigation transports these harmful chemicals to the habitats of no target animals. Chemicals can build up in the tissues of these animals, and when humans consume the animals the increased potency of the pesticides is manifested as health problems and in some cases death. Chemists have recently developed naturally occurring pesticides that are toxic only to their particular targets and are benign to birds and mammals. The most significant pesticide of the twentieth century was DDT, which was highly effective as an insecticide but did not break down in the environment and led to the death of birds, fish, and some humans.

2.0.2 Types of Pesticides

Bactericides for the control of bacteria.
Fungicides for the control of fungi and oomycetes.

Herbicides for the control of weeds.

Insecticides for the control of insects - these can be Ovicides, Larvicides or Adulticides.

Miticides for the control of mites

Molluscicides for the control of slugs and snails.

Nematicides for the control of nematodes.

Rodenticides for the control of rodents.

Virucides for the control of viruses.

Pesticides can also be classed as synthetic pesticides or biological pesticides, although the distinction can sometimes blur.

2.1 The Potential for Biopesticides and their consumption in India

About 80,000 tons of pesticides are used in agriculture in India annually (Srinivasan, 1997), mostly in cotton and rice. While cotton is planted on about 5% of the total Cultivable area (on about 8 million hectares out of a total of 170 million), it accounts for about 45% of pesticide application (Dhaliwal and Pathak, 1993). Rice accounts for another 23%.Vegetables and fruit also account for a significant proportion(**T 2.1**)showing crop wise consumption of pesticide.

CROPS	PESTICIDE CONSUMPTION IN %AGE
Cotton	44.5
Paddy	22.8
Jowar	8.9
Fruits and vegetables	7.0
Wheat	6.4
Arhar	2.8
Other	7.6

T 2.1 – Showing cropwise consumption of pesticide in India (%)

The intensive use of pesticides in agriculture is a cause of serious concern. The problem is especially serious because of the development of resistance to pesticides in important pests and the presence of pesticide residue in agricultural and dairy products. Pesticide resistance has mainly been caused by excessive and indiscriminate use of pesticides (Jayaraj, 1989) Pesticides of spurious quality, which are commonly sold in small towns and villages, have also contributed to resistance in many areas products the other important problem caused by the excessive and inappropriate use of chemical pesticides concerns the presence of pesticide residue in food. Many of the pesticides currently being used have a tendency to survive in plants for a long time. They also enter the food chain and are found in metal and dairy products. The problem of pesticide residue is already a serious threat to health and environment in India. The incidence For example, according to one study, more than 80% of milk samples tested in India was found to contain residues of pesticide DDT and HCH residue is much higher in India than in developing countries. (Handa,).

According to another study, residue of DDT and benzene-hexachloride suspected carcinogens, were found in the breast milk samples collected from mothers in Punjab. The amount of residue was very high and babies were ingesting 21 times the amount of these chemicals considered acceptable through their mother's milk (Jumanah, 1994)

2.2 Pesticide Properties

Properties that affect a pesticide's potential to pollute water include formulation, toxicity, persistence, volatility, solubility in water, and soil adsorption. Of course, pollution risk also is affected by soil characteristics, application methods, weather and other factors.

2.2.1. Toxicity

The active ingredient is the chemical compound in a pesticide that kills or otherwise affects the target pest. Other substances in a pesticide formulation are inert ingredients that act as carriers and preservatives for active ingredients, and also make mixing and application easier. When determining whether and how to register a pesticide, the EPA considers the toxicity of the active ingredient. Toxicity is determined by the amount required to produce biological effects.

2.2.2 Dose and Effective Dose

A dose is the amount of a substance used at one time. Most substances are toxic at large enough doses, but harmless or even beneficial at lower doses. Drinking water is an example. People need to drink some water every day. However, drinking the equivalent of 15 percent of one's body weight can be fatal. Similarly, table salt is absolutely necessary for proper health, but as little as 1 ounce (2 Tablespoons) of table salt would deliver a lethal dose to a 1-year-old child. There is a lethal dose of caffeine in 100 cups of coffee. There is a lethal dose of alcohol in a quart of whiskey. There is a lethal dose of oxalic acid in 20 pounds of spinach. There is a lethal dose of aspirin in 100 tablets. We can compare aspirin with two chemical pesticides.

Malathion is about half as toxic as aspirin. Parathion is 70 times more toxic than aspirin. The hazards of pesticide residues are negligible compared to the dangers from common household chemicals and medicines.

Table (**T 2.2)** compares toxicities of common products with pesticides. The effective dose is the amount of a substance needed to kill or otherwise affect a target pest. Amounts less than the effective dose will likely not kill the target pest. Amount greater than the effective dose will not necessarily be more effective in killing the target pest. Instead, this larger dose may kill more non-target organisms, cost more, and pollute the environment.

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 (rodenticide)	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)
Allethrin (insecticide)	1,160	Gasoline
Diazinon (insecticide)	1,250	Tobacco
Malathion (insecticide)	5,500	Castor oil
Ferbam (fungicide)	16,900	Mineral oil
Methoprene (hormone)	34,600	Sugar

T 2.2 - Showing the comparative study of pesticides and natural products.

Common measures of a chemical's toxicity are the LD50 and LC50. These measures refer to doses that kill 50 percent of the animals in a test group. These toxicity terms can apply to target pests or non-target organisms, including humans. The toxicity of a substance determines its proper dosage.

2.2.3 Persistence

Persistence describes how long a pesticide remains active. Half-life is one measure of persistence. The half-life of a substance is the time required for that substance to degrade to one-half its original concentration. In other words, if a pesticide has a half-life of 10 days, half of the pesticide normally breaks down by 10 days after application. After this time, the pesticide continues to break down at the same rate.

The half-life of a pesticide is not an absolute factor. Soil moisture, temperature, organic matter, available oxygen, microbial activity, soil pH, photo degradation and other factors may cause the half-life of a substance to vary.**(T 2.3)** Showing the MLCs for pesticide found in drinking water. In general, the longer a pesticide persists in the environment, the more likely it is to move from one place to another and be a potential source of pollution.

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 2.3 – Showing MCLs for pesticides found in drinking water.

2.2.4 Volatility

Many pesticides, including several types of herbicides and soil fumigants can escape from soils as gases some can distil from soils and enter the atmosphere with evaporating water. Pesticide particles in the atmosphere can come back to earth in rain or snow, and then either leach into ground water or be carried by runoff into surface waters.

2.2.5 Water Solubility

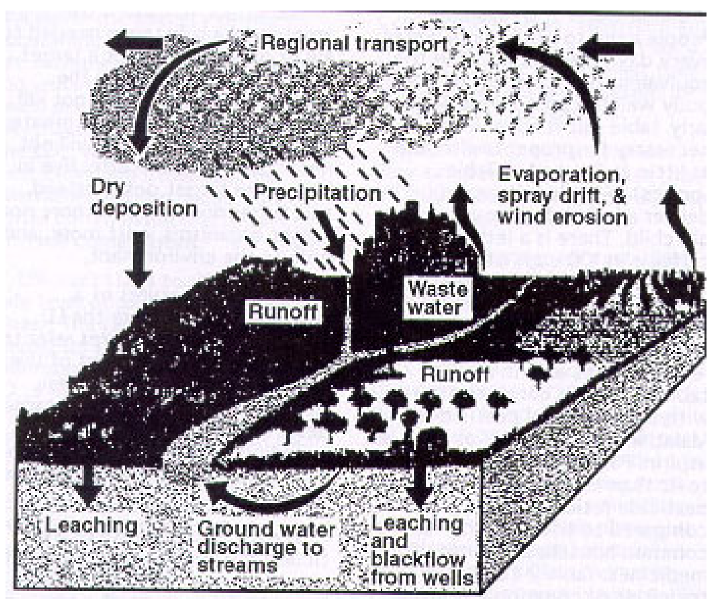
The water solubility of a pesticide determines how easily it goes into solution with water. When these compounds go into solution with water they can travel with it as it runs off the land or leaches through the soil. The solubilities of materials such as pesticides are usually given in parts per million (ppm), or in some cases as milligrams per liter (mg/l). The solubility of a substance is the maximum number of milligrams that will dissolve in 1 liter of water.

2.3 Mode of entry of pesticides in water

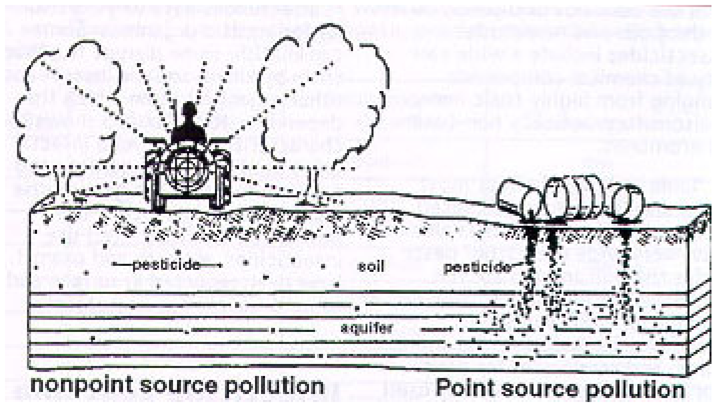
The over-application or misuse of pesticides and other agricultural chemicals (such as fertilizers) can allow these chemicals to enter surface and ground water. Drift, evaporation and wind erosion can carry pesticide residues into the atmosphere. From there they can fall in rain or snow to contaminate 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.

Agricultural chemicals also can pollute surface water through irrigation return flow and rainfall runoff. Carefully following label directions about proper dosage and application methods can greatly reduce the possibility of water contamination. Pesticides can enter water through surface runoff, leaching or erosion. Water that flows across the surface of the land, whether from rainfall, irrigation, snow melt or other sources, always flows downhill until it meets a barrier, joins a body of water, or begins to percolate into the soil. Some pesticides and fertilizers can be carried along with runoff. Wind and water can erode soil that contains pesticide residues and carry them into nearby bodies of water. Even comparatively insoluble pesticides and pesticides with high soil adsorption properties can move with eroding soil.

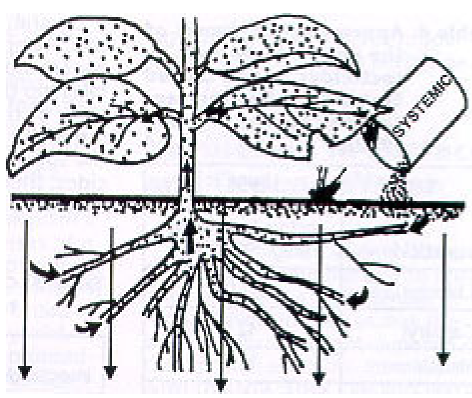
Pesticides that enter water supplies can come either from point sources or from non-point sources. Point sources are small, easily identified objects or areas of high pesticide concentration such as tanks, containers or spills. Non-point sources are broad, undefined areas in which pesticide residues are present. Now a days, due to excessive use of the pesticides for the increased productivity leading to the infertility of soil, and besides this, also causing different pollution problems such as surface water, ground water, soil pollution. The **(Figures 2.1, 2.2, 2.3, 2.4)** shown below describe about the different modes of movement of pesticides and the pollution created.



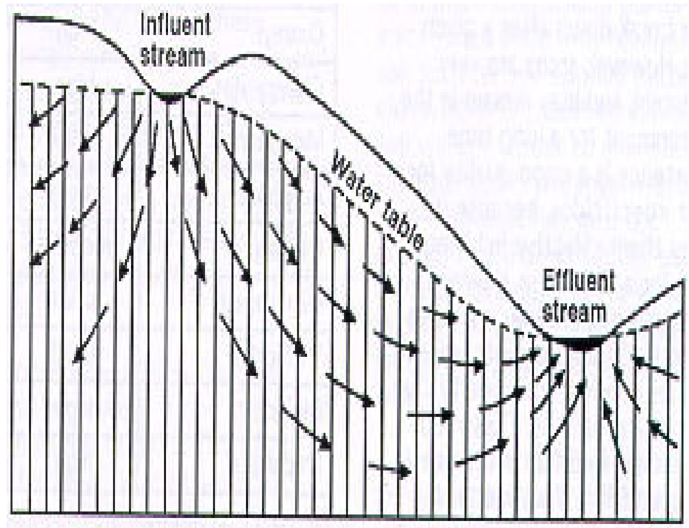
F 2.1 - Showing pathways of pesticide movement in the the hydrological cycle.



F 2.2 - Showing point and non-point source pollution.



F 2.3 - Showing water soluble pesticides leach more readily into ground water.



F 2.4- Showing percolation can transport water soluble pollutants from one body of water to another.

2.4. Pesticide Pollution

2.4.1 Pesticide pollution

Pesticides are the chemicals used to kill the pests. Environmental Protection Agency (EPA) estimates that the use of pesticides doubled between 1960 and 1980. Currently, over 372 million kilograms a year are used in the United States, with over 1.8 billion kilograms a year used worldwide.

2.4.2 Biomagnification

Biological magnification also called as biological concentration or bioaccumulation, is characterized by the increase in the toxic substances in successive tropics levels of a food chain.

2.4.3 Quality Control

DDT is the most widely noted case of a pesticide that caused damage far from the farm. High levels of DDT have been found in birds of prey, causing them to become endangered because of the effect it has on their eggs. **(T 2.4)** Showing the pesticide % age in different fruits.

Fresh Fruit and Vegetables	Number of Samples Analyzed	Samples with Residues Detected	Percent of Samples with Detections	Different Pesticides Detected	Different Residues Detected	Total Residue Detections
Apples	774	727	98	33	41	2,619
Lettuce	743	657	88	47	57	1,985
Pears	741	643	87	31	35	1,309
Orange Juice	186	93	50	3	3	94

T 2.4 – Showing pesticides percentage in different fruits

DDT becomes more concentrated the higher it climbs in the food chain, and many people have voiced their concern about its possible presence in humans. In 1972, the Environmental Protection Agency (EPA) announced a ban on almost all uses of DDT.

2.5 Water Quality Protection

Most water pollution does not come from the normal, correct usage of pesticides. Problems arise from misuse or careless handling. Here is a checklist to use when applying any pesticide. These guidelines can help safeguard the future of our water quality.

- Read all product labels and follow label directions.
- When possible, use pesticides and fertilizers with less potential for surface runoff or leaching.

- Use integrated pest management (IPM) tactics to control pests, using pesticides only when necessary.

- Don't apply pesticides when conditions are most likely to promote runoff or excessive leaching.
- Have soil tested to determine the fertilizer needs of a given crop.
- Store potential water pollutants away from water sources such as wells, ponds and streams.
- Prevent pesticide spills and leaks from application equipment.
- Make sure product containers do not leak.
- Do not dispose of leftover materials by dumping them in drains or on the ground.
- Dispose of pesticides according to label directions.
- Use low-toxicity products when a choice is possible.

CHAPTER 3
REVIEW OF LITERATURE

3.0 Overview

Organ phosphorus pesticides make up of one of the most important groups of insecticides applied to pest control. Substantive application of pesticides may cause contamination in the hydrological systems (Meyer & Thurman, 1996) and pesticides residue in food crops (Adeyeye & Osibanjo, 1999; Hura, Leanca, Rusu, & Hura, 1999) Pesticides have been considered to be potential chemical mutagens and pesticide residues, such as DDT, diazinon and parathion, in vegetables and fruits are widely concerned due to their potential chronic health impacts (Bolognesi & Morasso, 2000). A number of physical–chemical and conventional methods, such as Fenton oxidation (Wang & Lemley, 2002), biotreatment (Liu et al., 2004), TiO_2 catalytic treatment (Kouloumbos, et al., 2003), powdered activated carbon filtration and reverse osmosis have been demonstrated to be highly effective for the removal of organic chemicals including pesticides (Heijman & Hopman, 1999). Those techniques mainly focused on pesticides dissolved in aqueous solutions. However, they are less effective or unsuitable for removal of residual pesticides adhering on vegetable surface. Four pesticides, methyl-parathion, parathion, diazinon and cypermethrin were commonly used as broad-spectrum insecticides in crop pest control, and high residual levels had been detected in vegetables (Ma, Peng, & Liu, 2003; Tong, 1994). Parathion and its methyl analog are probably the most widely used organophosphorus insecticides in agriculture. Methyl-parathion is a persistent pesticide commonly found in trace levels in the environment (Couper, Manning, Forman, Goolsby, & Majewski, 200

3.1 Water Treatment Processes and Removal Efficiencies

3.1.1 Conventional Treatment

A typical system for surface water treatment generally consists of pre-settling, coagulation/flocculation (sediment removal), granular filtration (sediment removal), corrosion control (pH adjustment or addition of corrosion inhibitors), and disinfection

(J.M.M. Consulting Engineers, 1985; Faust and Aly, 1999; USEPA, 1989). It is important to note there are many variations on this common sequence, regarding points of addition of a wide variety of chemicals (e.g., chlorine, ammonia, ozone, coagulants, filter aids, PAC, etc.). The pre-settling process is a preliminary removal of materials (including non-colloidal sediment) from the raw water. The water is then treated with alum and polymers to encourage flocculation of the colloidal materials (including suspended sediment) and then allowed to settle. Next, the water is passed through a granular filter comprised of sand and possibly anthracite. After filtering, the water is conditioned to prevent corrosion and then disinfected using either chlorine or chloramines.

3.1.2 Coagulation/Flocculation

Coagulation and flocculation is a two-step process to remove inorganic and organic colloidal materials from water. Colloidal materials are particles that are so small (less than 10 μm) that they stay suspended in the water. They often have charged surfaces that cause them to repel each other. The coagulation process neutralizes the colloid's surface charge, which is then followed by mixing, and eventually causes flocculation (the joining of individual particles) of the colloids into aggregates called "flocs". The flocs are then large enough to settle from the water column. This process is needed to remove turbidity (inorganic colloids) and color (organic colloids). Removal of organic colloids such as humic and fulvic acids is critical because they are known precursors to the formation of disinfection by-products (e.g., trihalomethanes) when chlorine is added.

3.1.3Adsorption Process

Addition of powdered activated carbon to, or with, the addition of coagulant for organic removal. Miltner et al. (1989) provide information on the possible removal of pesticides with conventional treatment. In this study, three triazine pesticides (atrazine, simazine, and metribuzin), two acetanilides (alachlor and metolachlor), linuron, and carbofuran were were removed by the conventional treatment process. Chen et. al (2001) reported photo oxidation, photoreduction and adsorption occur on or near the particle surface and toxic pollutants or compounds get adsorbed on the surface. The initial concentrations of the pesticides as shown in **(T 3.1)**, range from 34.3 to 93.4 μg/L. After alum coagulation

$(SO_4)_3 14H_2 0$: 15-30 mg/L], the initial turbidity of the raw water (6 - 42 NTU, Nephelometric Turbidity Units) dropped to less than 1 NTU in the settled water. **(T 3.1)** shown below summarizes the data obtained on the possible removal of the six pesticides during alum coagulation. No removal of the triazine pesticides, linuron, and carbofuran was observed. The removal of alachlor and metolachlor was low and ranged from 4 to 11 % percent.

Pesticide	**Coagulation(mg/l)**	**Initial conc.(ug/l)**	**% Removal**
Atrazine	Alum (20)	65.7 (SW)*	0
Simazine	Alum (20)	61.8 (SW)	0
Metribuzin	Alum (30)	45.8 (SW)	0
Alachor	Alum (15)	43.6 (SW)	4
Metolachor	Alum (30)	34.3 (SW)	11
Linuron	Alum (30)	51.8 (SW)	0
Carbofuran	Alum (30)	93.2 (SW)	0

T 3.1 - Showing the six pesticide removal by the process of alum coagulation.

Carbon adsorption is an advanced wastewater treatment method used for the removal of recalcitrant organic compounds as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. The adsorption of nitrobenzene (NB) and phenol onto activated carbon has been widely studied. Both (NB and phenol) showed to be well adsorbable compounds onto activated carbon but in low concentration (Cañizares et al., 1999; Sacher et al., 2001). This method has been also combined with other and a significant improvement has been obtained (Cañizares et al., 1999). Most of them showed the high effectiveness of carbon activated adsorption process in the reduction of COD (Chemical Oxidation Demand).

3.1.4. Incineration

The incineration is a useful method for small quantities of wastewater with high pollutant concentration. However, it presents the disadvantage of requiring big investments and having high energy cost as well. The treatment of phenolic effluents by means of this method has been reported (Lanouette, 1977).In the case of textile activities, the incineration has been used in the treatment of sludge from textile wastewater and the ash is landfilled (Masselli et al., 1970).The incineration can be also used to minimize the textile wastewater quantity and after other treatment processes could be applied. According to the recent report (Gordan L. Nelson, 2000) a number of pesticides, insecticides, herbicides were treated by this process and the toxic pesticides were listed under the TOXFIRE technology were incinerated based on their incineration properties, ignition point.

3.1.5 Air stripping

Air stripping involves the transfer of volatile organics from liquid phase to the air phase by greatly increasing the air/water contact area. Typical aeration methods include packed towers, diffusers, trays, and spray aeration. It has the advantage that is more established and more widely understood technology than chemical oxidation. It can be accurately designed from theory and experience without the need for design tests. Taking into account that the dichloroethyl ether (DCDE) is a volatile compound, air stripping can bethought as treatment method for this compound. However, air stripping has been used in the treatment of trichloroethylene (TCE), dichloromethane (DCM), 1,2-dichloroethylene (DCE), 1,2-dichloroethane (DCA), chlorobenzene (Cl-Bz), and DCEE and the results showed that they could be removed easily from water solutions except DCEE (Li et al., 2000).

3.1.6 Wet oxidation

In the wet oxidation processes, organic and inorganic compounds are oxidized in aqueous phase, with oxygen or air, at high pressure and high temperature conditions. The temperature depends on the nature of the compounds to degrade, however it oscillates between 150 and 350ºC. Pressure goes from 20 to 200 bars. COD removal ranges from 75 to 90% (Li et al., 1991). The mechanism of wet oxidation has been deeply studied and seems to take place by means of a free radical process. Compounds contain halogen and nitro functional groups have been found to be difficult to be degraded by this method (Scott, 1997).

3.1.7 Electrochemical oxidation

The use of electrochemical oxidation for the destruction of organic compounds in water solutions has been tried on bench and pilot plant scale (Mieluch et al., 1975; Boudenne et al., 1996; Brillas et al., 1998b), but is not used commercially because of its high operating cost. The use of electrochemical oxidation for the destruction of organic compounds in water solutions has been tried on bench and pilot plant scale (Mieluch et al., 1975; Boudenne et al., 1996; Brillas et al., 1998b), but is not used commercially because of its high operating cost. The mechanism of the electrochemical processes involves three stages: electrocoagulation, electroflotation and electrooxidation.Few studies have been found in the literature regarding the electrochemical oxidation of NB (Comminellis, 1994; Colucci et al., 1999) However, for phenol solutions many works recommend the use of this method for their treatment (Lanouette, 1977; Smith, and Watkinson, 1981; Comninellis and Pulgarin, 1993; Pulgarin et al., 1994). In many of them, the efficiency of this method for color removal has been proven (Lin and Peng, 1994; Vlyssides et al., 2000; Zappi et al., 2000; Gutierrez et al., 2001). It has been also used in combination with coagulation to remove color, turbidity and COD.

3.1.8 Biological oxidation

Biological treatment, generally by means of activated sludge (Wiesmann and Putnaerglis, 1986; Givens et al., 1991), in adequate conditions (Wu et al., 1994) has unquestionable advantages for the destruction of organic compounds. However, many organic pollutants cannot be effectively eliminated by biological oxidation in the treatment of municipal or residual waters nor natural waters (Bishop et al., 1968). Its application to the treatment of effluents with phenols, nitro aromatic, ether aliphatic compounds and textile waters is quite restricted because of the high toxicity inherent in these wastes, the need to adjust the pH to an adequate value and add food and oxygen in adequate quantities for the transforming microorganisms (González, 1993), as the viability of the process depends fundamentally on the health and activity of the latter. There are two kinds of processes in the biological treatment of biological compounds: aerobic and anaerobic (Eckenfelder et al., 1989; Wang, 1992). The aerobic processes are used more because of their efficiency and operational simplicity (Ruiz et al., 1992). Killing microbial cells through the use of photoexcited semiconductor powder was first reported by Matsunaga and co-workers in 1985. Seignez and Coworkers (1992) these authors reported a decrease of 20% of the initial COD value of an organic compound degradation involves a primary structural chance of the initial organic molecule, while a COD abatement of 70% represents a complete mineralization as the end products are small that can be biologically degraded.

3.1.9 Chemical oxidation

Oxidation, by definition, is a process by which electrons are transferred from one substance to another. This leads to a potential expressed in volts referred to a normalized hydrogen electrode. From this, oxidation potentials of the different compounds are obtained (Beltrán et al., 1997; Munter et al., 2001). Chemical oxidation appears to be one of the solutions to be able to comply with the legislation with respect to discharge in a determined receptor medium. It can also be considered as an economically viable previous stage to a secondary treatment of biological oxidation for the destruction of non-biodegradable compounds, which inhibit the process. The optimization of the process (Akata and Gurol, 1992) arises in those conditions in which non-biodegradable material is eliminated, but with a minimum amount of oxidizer.

3.2 ADVANCED OXIDATION PROCESSES

For the oxidation of organic pollutants, a series of researchers have proposed direct photooxidation with ultraviolet light (Petersen et al., 1988). A large amount of studies (Legrini et al., 1993) dealt with the degradation of chemicals in water using the Hg emission at 253.7 nm produced by low-pressure mercury lamps. However, results showed that 253.7 nm irradiation alone could not be used as an effective procedure for the removal of organics from water: it may be useful for the degradation of substituted aromatic, however it is totally inefficient for effective removal of chlorinated aliphatic. In the photochemical reactions, hydroxyl radicals may be generated by water photolysis (Cervera and Esplugas, 1983):

$$H_2O \xrightarrow{h\upsilon} H^{\cdot} + OH^{\cdot}$$

Photolysis involves the interaction of light with molecules to bring about their dissociation into fragments. This reaction is a poor source of radicals, and in the reaction medium large quantity of reaction intermediates that absorb part of the radiation are generated, which decreases considerably the photooxidation kinetics of the contaminants. That fact makes the process valid only for effluents with low concentration of pollutants.

The photochemical treatment, although partially solving the problem of the refractory compounds, has some negative aspects in its practical application, as the high cost of UV radiation production. Furthermore, not all the emitted radiation is used, only the absorbed radiation and only a fraction of this radiation produces chemical changes. This fact makes that some photodegradation reactions have a very low yields and slow kinetics. To accelerate the process, other oxidants like hydrogen peroxide and/or ozone, metallic salts or semiconductors like TiO_2 can be added, giving rise to the so-called advanced Oxidation Processes. Instead of UV lamps, solar light could be used as radiation energy to degrade some compounds. No effect was observed during direct photolysis of NB with a 150-W mercury xenon lamp in the study carried out by (Lipczynska-Kochany, 1992).

3.2.1 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. Paillard et al. (1998) studied the elimination of atrazine in filtered water. Results showed better degradation of the pesticide 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) established 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 advantage of selective molecular ozone reactions before converting the process to non-selective free radical attack.

3.2.1 Ozone–UV radiation (O_3/UV)

The use of O_3/UV system brings about complete and fast mineralization of organic compounds present in complex structure of pesticides with a short molecular chain (glyoxal, glyoxylic acid, oxalic acid, and formic acid) can be achieved according to Gurol & Vatistas (1987) and Takahashi (1980). Peyton et al. (1982) demonstrated the efficiency of O_3/UV system for C_2Cl_4 elimination from water compared to ozonation and photolysis only.

3.2.2 Photo-Fenton and Fenton-like systems

When Fe^{3+}ions are added to the H_2O_2/UV process, the process is commonly called photo-Fenton-type oxidation. At pH 3, the Fe $(OH)^{2+}$ complex is formed because of the acidic environment:

$$\mathbf{Fe^{3+} + H2O \rightarrow Fe\ (OH)^{2+} + H^+}$$
$$\mathbf{Fe\ (OH)^{2+} \longleftrightarrow Fe^{3+} + OH^-}$$

When exposed to UV irradiation, the complex is further subjected to decomposition and will produce $^{\cdot}OH$ and Fe^{2+} ions:

$$\mathbf{Fe\ (OH)^{2+} \rightarrow Fe^{2+} + OH}$$

Fenton and photo-Fenton process have been used with great success for the degradation of several organic and inorganic pollutants including pesticides (Malato Blanco et. Al; Parra, Malato et. al 2002; Fare et al. 2005). The optimum application of the Fenton/photo Fenton processes holds at pH between 2.5 and 4 (Gallard H. 1998).

According to annual report of pesticides 97, a Fenton catalyst is possible in PSA reactors. 500 mg TOC/L of pesticides are 80% destroyed in 3 hours using PSA-CPCs field**.** Sun & Pignatello (1993) showed that a number of herbicides and pesticides (like malathion, parathion) can be totally mineralized by the hν–Fe (III)/H_2O_2 process, and the mineralization of chlorophenol by the photo-Fenton process was demonstrated by Ruppert et al. (1993).

Fares et.al (2007) reported pesticide (Vydine) in solar photo-Fenton reaction produced higher pesticide degradation (88% pesticide removal) in a shorter time (40 minutes)

3.2.3 Photo catalytic Oxidation (UV/TiO_2)

The basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation,Weichgrebe (1994) indicated that photocatalytic oxidation is the best in terms of the process rate under the conditions of pH 3.0 (pH 3.0, 5.0, 7.0, and 11.0 were tested) when landfill leachate is treated by either H_2O_2/UV or TiO_2/H_2O_2/UV. Way & Wan (1991) found that acidic conditions with pH value less than 2 do not favour the photocatalytic oxidation of phenol and a number of complex structure pesticides.Marinas (2001) described in literature that Formetanate a common insecticide showed better degradation by the photo catalytic process using new cascade falling film photo reactor (STEP).

Ollis et.al (1991) reported that a number of herbicides and pesticides that may contaminate water such as 2, 4, 5-trichlorophenoxyacetic acid, 2, 4, 5-trichlorophenol, s-triazine herbicides and DDT can also be mineralized into harmless products by photo catalysis.Photocatalytic processes have been investigated by many other researchers also, Ahmed and Ollis (1984) and Matthews, 1987) showed that sunlight-activated titanium dioxide catalyst can initiate the complete oxidation of organic chemicals. Examples of organic compounds that can be destroyed by this process are pesticides, dioxins, chlorinated solvents.

CHAPTER 4
ADVANCED OXIDATION PROCESSES (AOPs)

4.0 Introduction

In the near future, advanced oxidation processes (AOPs) may become the most widely used water treatment technologies for organic pollutants not treatable by conventional technologies due to the high chemical stability and/or low biodegradability of such pollutants. These processes involve generation and subsequent reaction of hydroxyl radicals (·OH). Many oxidation processes, such as TiO_2 /UV, H_2O_2 /UV, Photo-Fenton, and ozone O_3, O_3 /UV, O_3/H_2O_2 are currently employed for this purpose. Hydroxyl radicals attack is not very selective, which is a useful attribute for use in pollution treatment. Advanced oxidation processes (AOP's) have been applied for water purification in recent years, which are promising for the degradation of toxic and bio-resistant organic pollutants in aqueous solution. After fluorine, the hydroxyl radical is the second to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions. The reactions by which hydroxyl radicals attack organic molecules are hydrogen abstraction, electrophilic addition, electron transfer and radical – radical reactions. Different combinations of homogeneous and heterogeneous methods using ozone, hydrogen peroxide, UV radiation and titanium dioxide, combination of hydrogen peroxide with ferrous ions (Fenton reagent) are known to produce these radicals. The ($^{\cdot}OH$) radicals are generated in solution and due to its strong oxidative nature; they are responsible for the oxidation of organic compounds mainly by hydrogen generating free organic radicals R.$^{\cdot}$

$$^{\cdot}OH + RH \longrightarrow R^{\cdot} + H_2O \quad (1)$$

These latter radicals can react with molecular oxygen forming peroxy radicals.

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \quad (2)$$

$$RO_2^{\cdot} \longrightarrow \textbf{Products} + CO_2 \quad (3)$$

Starting a series of oxidative degradation reactions that can lead to complete mineralization of the organic compound. The above-mentioned combined methods for **$^{\cdot}$OH** radical production are of special concern as some of them can use solar energy also which is a solution for the limitation of high cost of AOP's. But it is possible only for iron and titanium dioxide catalyzed homogeneous and heterogeneous photochemical reactions respectively. These catalysts absorb at wavelengths of solar spectrum alike hydrogen peroxide and ozone. Since hydroxyl radical generation is the key step in oxidation, oxidation potential of common oxidants are important to be known **(See T 4.1)**

Species	Oxidation potential (v)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic Oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permagnate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49

T 4.1 - Showing oxidation potential of various species.

Hydroxyl radical generates organic radicals on reaction, which yield peroxyl radical, and further initiating chain reaction of oxidations, leading finally to carbon dioxide, water and inorganic salts **[Reaction (1)(2)&(3)].**Besides hydrogen abstraction, electron transfer to hydroxyl radical is another mechanism of oxidative degradation **[see reaction (4)].**

$$^{\cdot}OH + RH \longrightarrow RH^{\cdot +} + OH^{-} \quad (4)$$

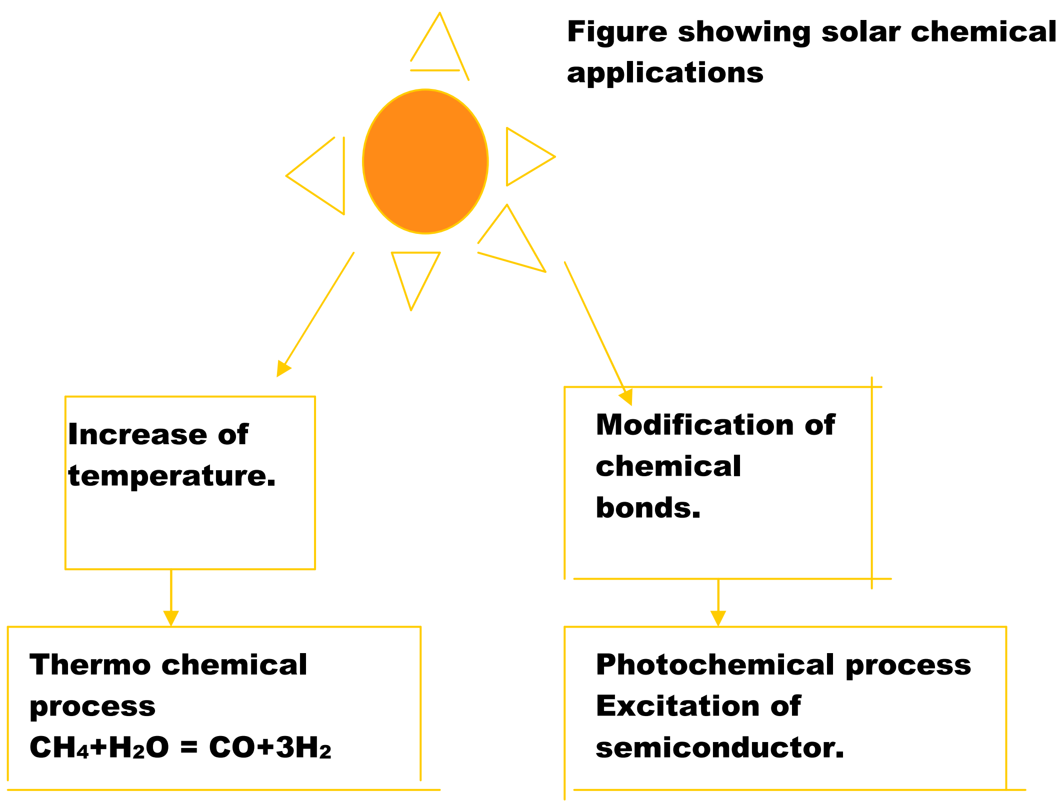
Wu (1998) summarized principles and advantages of several AOP systems.

4.1 Solar Chemistry

In this there are two main technologies which are discussed these are thermo chemical processes and photochemical processes.

4.1.1 Thermo chemical processes---- in this process solar radiation is converted into thermal energy that causes a chemical reaction. Such a chemical reaction is produced by thermal energy obtained from the sun for the general purpose of substituting fossil fules.

4.1.2 Photochemical processes----- solar photons are directly absorbed by reactants and catalyst causing a reaction this path leads to a chemical reaction produced by the energy of the sun's photons, for the general purpose of carrying out new processes.



F 4.1 - Showing solar chemical applications.

The term photo catalysis implies the combination of photochemistry with catalysis. Both light and catalyst are necessary to achieve or to accelerate a chemical reaction. Photo catalysis may be defined as the “acceleration of a photoreaction by the presence of catalyst”. Heterogeneous processes employ semiconductor slurries for catalysis, whereas homogeneous photochemistry is used in a single-phase system.

4.2 Types of AOP’s

4.2.1 Heterogeneous photo catalysis

In the case of heterogeneous photocatalysis, the interaction of a photon produces the appearance of electron/hole pairs, the catalyst being a semiconductor.Cristina Lizama Bahena and Susana Martinez (2006) reported that heterogeneous photocatalysis is a good method for the degradation of a number of pesticides such as (chlorbromuron, atrazine, and alachlor) in aqueous systems under non-expensive solar irradiation.

$$C \xrightarrow{h\nu} C(e - + h+)$$

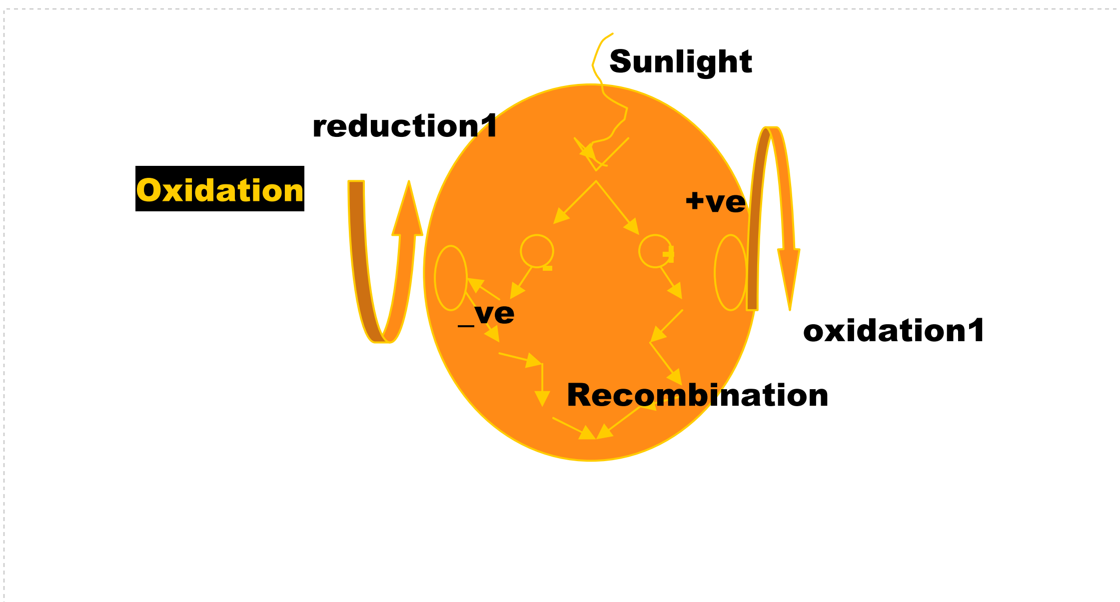
$$h^+ + Red_2 \longrightarrow Ox_2$$

$$e^- + Ox_1 \longrightarrow Red$$

→ (Heterogeneous reaction)

The concept of heterogeneous photo catalytic degradation is simple: the use under irradiation of a stable solid semiconductor for stimulating a reaction at the solid/solution interface. During photo excitation (a forms from the bulk of the semiconductor and the bands bending provides the conditions for carrier separation in the case of semiconductor particles, there is no ohmic contact to extract the majority carriers and to transfer them by an external conductor to a second electrode. This means that the two charge carriers should react at the semiconductor/electrolyte interface with the species in solution. Under steady state conditions the amount of charge transferred to the electrolyte must be equal and opposite for the two types of carriers, the semiconductor mediated redox processes involve electron transfer across the interface. When electron/hole pairs are generated in a semiconductor particle, the electron moves away from the surface to the bulk of the semiconductor as the hole migrates towards the surface. If these charge carriers are separated fast enough they can be used for chemical reactions at the surface of the photo catalyst i.e., for the oxidation or reduction of pollutants. A semiconductor particle is an ideal photo catalyst for a specific reaction if:

- The products formed are highly specific.
- The catalyst remains unaltered during the reaction.
- The formation of electron/pairs is required (generated by the absorption of photons with energy greater than that necessary to move an electron from the valence band to the conduction band.)
- Photon energy is not stored in the final products, being an exothermic reaction and only kinetically retarded.



F 4.2 - Showing fate of electrons and holes within a particle of illuminated semiconductor in contact with an electrolyte.

4.2.2 Homogeneous photo degradation

The use of homogeneous photo degradation (single-phase system) to treat contaminated waters dates back to the early 1970s. Although the homogeneous aqueous systems that employed the sole sun irradiation produced a primary structural chance of the original molecule of each herbicide, mineralization was not achieved.

$$C \xrightarrow{h\nu} C^*$$

$$C^* + R \longrightarrow RE^* + C^*$$

$$R^* \longrightarrow P$$

→ (Homogeneous reaction)

However, photocatalysis in the presence of TiO_2 not only produced a primary structural change of the original molecule of each herbicide, but also produced the mineralization of the three organic compounds in a short time period by the employment of sun irradiation. The first applications concerned the use of UV/ozone and UV/H_2O_2. The use of UV light for photo degradation of pollutants can be classified in to two principal areas:

1. **Photo-oxidation.** Light driven oxidative processes principally initiated by hydroxyl radicals.
2. **Direct photodegradation**. Light – driven processes where degradation proceeds following direct excitation of the pollutant by UV light.

Photo oxidation involves the use of UV light an oxidant to generate radicals. The hydroxyl radicals then attack the organic pollutants to initiate oxidation three major oxidants are used: hydrogen peroxide (H_2O_2), ozone and photo-Fenton reaction.

The primary process for absorption of light below 365nm is dissociation to yield two hydroxyl radicals:

$$H_2O_2 \longrightarrow 2{*}OH$$

The use of hydrogen peroxide is now very common for the treatment of contaminated water due to several practical advantages. The H_2O_2 is available as an easily handled solution that can be diluted in water to give a wide range of concentrations.

- There are no air emissions.
- A high-quantum yield of hydroxyl radicals is generated.

The major drawback is the low molar extinction coefficient, which means that in water with high UV absorption the fraction of light absorbed by H_2O_2 may be low unless very large concentrations are used.

Homogeneous and heterogeneous aqueous systems of the herbicides of chlorbromuron, atrazine, and alachlor were irradiated with a nonexpensive solar irradiation using a photoreactor with recirculation. Photodegradation of these herbicides occurred in both aqueous systems; however the presence of TiO_2 clearly accelerated the degradation of the three herbicides in comparison with direct photolysis. Degradation was followed by measuring the chemical oxygen demand (COD) as a function of reaction time for each aqueous system. Over 90% of COD abatement in the heterogeneous aqueous system was obtained in a short time period showing that mineralization of chlorbromuron, atrazine, and alachlor was achieved (Cristina et al., 2006)

Photo-oxidation with H_2O_2 as an oxidant – [see reaction (1) to (4)]

$$H_2O_2 + h\nu \rightarrow 2\,{}^{\cdot}OH \quad (1)$$

$${}^{\cdot}OH + RH \rightarrow R^{\cdot} + H_2O \quad (2)$$

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

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad (4)$$

Advantages

1. Available as easily handled solution can be dilute to give various concentrations.
2. No air emissions.
3. High quantum yield of hydroxyl radicals.
4. Onsite storage.
5. Infinite solubility in water

Drawbacks

1. Low molar extinction coefficient at the near UV-region.
2. High cost of UV-C lamps.
3. Small absorption cross section of H_2O at 254 nm is a problem.
4. $^{\cdot}OH$ radicals trapped by HCO_3^- and CO_3^{2-} producing CO_3^{2-}, with low oxidation potential.

Legrini et al. and Jacob et al., (1992) studied degradation of some organic compounds in industrial wastewater with H_2O_2 and 125 Wt. pressure Hg are.

Photo-oxidation with Ozone as an oxidant- refer to reaction (1) to (5)

$$O_3 + H_2O + h\nu \rightarrow O_2 \quad H_2O_2 \quad (1)$$

$$H_2O_2 + h\nu \rightarrow 2^{\cdot}OH \quad (2)$$

$$O_3 + \text{substrate} \rightarrow \text{Direct oxidation} \quad (3)$$

$$O_3 \rightarrow O_2 + O(^1D) \quad (4)$$

$$O(^1D) + H_2O \rightarrow {}^{\cdot}OH + {}^{\cdot}OH \quad (5)$$

Advantages-

1. Higher absorption cross-section than at 254 nm.
2. Destruction of toxic and refractory organics and microbial populations.
3. Decolorization of bleaching waters.

4. Higher rates of degradation than UV or Ozone used alone.
5. Oxides partially Halogenated and unsaturated halogenated HCs.

Drawbacks -

1. O_3 does not absorb light at > 300 nm wavelength.
2. Low- pressure mercury lamps emitting short UV radiation (UV-C) required.
3. Low Ozone solubility in water.
4. Potential secondary reactions of the oxidative intermediates.

Gurol et.al, (1987) reported degradation of mixture of phenol compounds with this technique using 16-Wt low pressure Hg lamp. Yue et al., (1992) worked on pesticide degradation by UV-Ozone method. Glaze et al., (1987) recommended stirred tank photoreactor for UV-Ozone process.

Photo-oxidation with Fe^{3+}/H_2O_2 as an oxidant – [refer to reaction (1) & (2)]

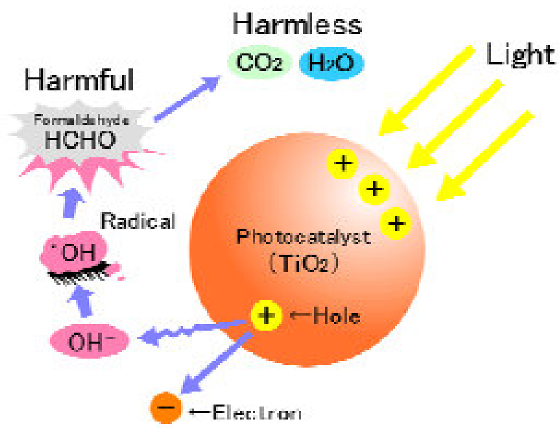
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{2+1} + OH^- + {}^{\cdot}OH \quad (1)$$

$$Fe^{3+} \rightarrow Fe^{2+} \quad (2)$$

4.3 Brief Introduction about Photo catalyst

4.3.1 What is Photo-catalyst?

Photo-catalyst produces surface oxidation to eliminate harmful substances such as organic compounds or nearby bacteria, when it is exposed to the sun or fluorescent lamp. By applying this principle to water treatment, dissolving NOx in the air, or room air purification, photo-catalyst can be used for various steps in purifying a contaminated environment.



F 4.3- Showing working of a photocatalyst.

The function of the photo-catalyst can be divided into five major categories as follows:

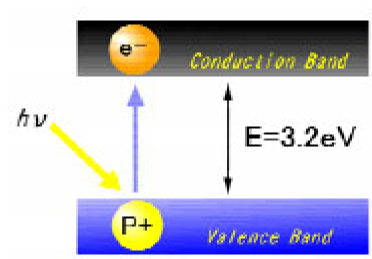
1. **Purifying water**
2. **Preventing contamination**
3. **Anti-bacteria**
4. **Deodorizing**
5. **Purifying the air (dissolving NOx)**

It might be well understood that the functions listed above are those which amplify or accelerate the functions of the sun, or ultra-violet radiation. In this sense, it is not strange to regard titanium dioxide as a photo-catalyst from the viewpoint that it works as the catalyst in accelerating the functions of the light.

4.3.2 What kind of light is necessary for the photo-catalyst?

As we explained, the photo-catalyst can be activated by light, so what kind of light is necessary for the photo-catalyst? There are various sources of light such as the sun, incandescent lamps, fluorescent lamps, light traps, disinfectant light, and so on. Those sources emit lights with different wavelengths necessary for their specific purposes.

TiO_2 is a semiconductor which turns to a high-energy state by receiving light energy, and releases electrons from its illuminated surface. If the energy received at this stage is high enough, electrons that were initially located in the so-called 'valence band' all jump up to the 'conduction band'.



F 4.4- Showing energy band

Thus, the energy that makes electrons jump up is provided by light, and this light energy is believed to be the energy of the light's wavelengths. Therefore, calculating from the height that the electrons have to jump up, this light should have the same wavelength as ultraviolet light.

E = h*ν*, E: energy **h:** Plank's constant ***ν:*** frequency

ν **= c / *λ* c:** light speed ***λ:*** wavelength

Therefore, **E** = ***hc / λ***

Here, E is titanium dioxide 3.2 eV (3.2 eV = $3.2 \times 1.6 \times 10^{-19}$ J), and if you substitute the determinate values *c*: 3.0×10^{8} m/s, *h*: 6.63×10^{-34} Js^{-1} , you will find out that the necessary wavelength is approx. 380 nm, which tells us that the light needed to activate Photocatalyst is ultraviolet light.

4.3.3 TiO_2 as better photo catalyst

TiO_2 is unexceptionally most suitable catalyst, having following unique properties:-

1. Inert (chemically and biologically).
2. Stable to corrosion.
3. Better from safety point of view.
4. Having low cost, limits the choice of convenient alternatives.
5. TiO_2 is of special interest as it can use natural UV.
6. An appropriate gap b/w valence and conduction band.
7. Band gap energy = 3.2 eV (VB energy = 3.1 eV & CB energy = -0.1 eV)
8. Absorbs in near UV light (<387 nm) (i.e., natural (solar) energy)

Comparison with other semiconductors

1. ZnO dissolved in acidic solutions.
2. CdS & GaP degraded during repeated catalytic cycles.

4.3.4 TiO_2/UV process

Carey et al. (1976) reported degradation of organic wastewaters with the help of TiO_2. TiO_2 can decompose various organics in water. Matthews et al., (1990) reported action of TiO_2 suspensions to improve detoxification of hazardous wastewater. Spectral absorption characteristic of tio_2 allow its extinction in UV-A, B & C regions, giving space for use of medium pressure mercury arcs. Photo excited TiO_2 has strong oxidative potential for holes (illustrated by reaction (a) given below).

$$TiO_2 + hv \rightarrow TiO_2\,(e^-\ h^+) \qquad (a)$$

Oxidation reactions taking place:-

1. Electron transfer from absorbed substrate- **[refer reaction no. (1)]**

$$TiO_2\,(h^+) + RX_{ad} \rightarrow TiO_2 + RX_{ad}^{\cdot +} \qquad (1)$$

Electron transfer from absorbed solvent molecule – [see reaction (1) &(2)]

Mostly occurring reaction because of higher concentration of H_2O & OH^-

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + OH_{ad}^- + H^+ \quad (1)$$

$$TiO_2 (h+) + OHad^- \rightarrow TiO_2 + {}^{\cdot}OHad \quad (2)$$

2. Molecular O_2 is electron-accepting species from conduction band – [reaction (1)]

$$TiO_2 (e^-) + O_2 \rightarrow TiO_2 + {}^{\cdot}O_2^- \quad (1)$$

3. Addition of H_2O_2 enhances rate of photo degradation- **[refer to reaction (1)]**

$$TiO_2 (e^-) + H_2O_2 \rightarrow TiO_2 + {}^{\cdot}OH + OH^- \quad (1)$$

Organic molecules adsorbed on surface of the TiO_2 are oxidized by ${}^{\cdot}OH$. Mills et al., (2002) used thick titanium films for semiconductor photo catalysis.

4.3.4.1 Advantages of UV/TiO_2 Process

- Large number of organic compounds in aqueous solutions can be degraded completely.
- Rate of reaction directly proportional to surface of catalyst.
- UV lamps are easily available (emitting in spectral region).
- Absorption cross-section on Tio_2 can be improved by surface modifications.
- Operational in UB-A region, maximum potential use of solar radiation.

Important specifications

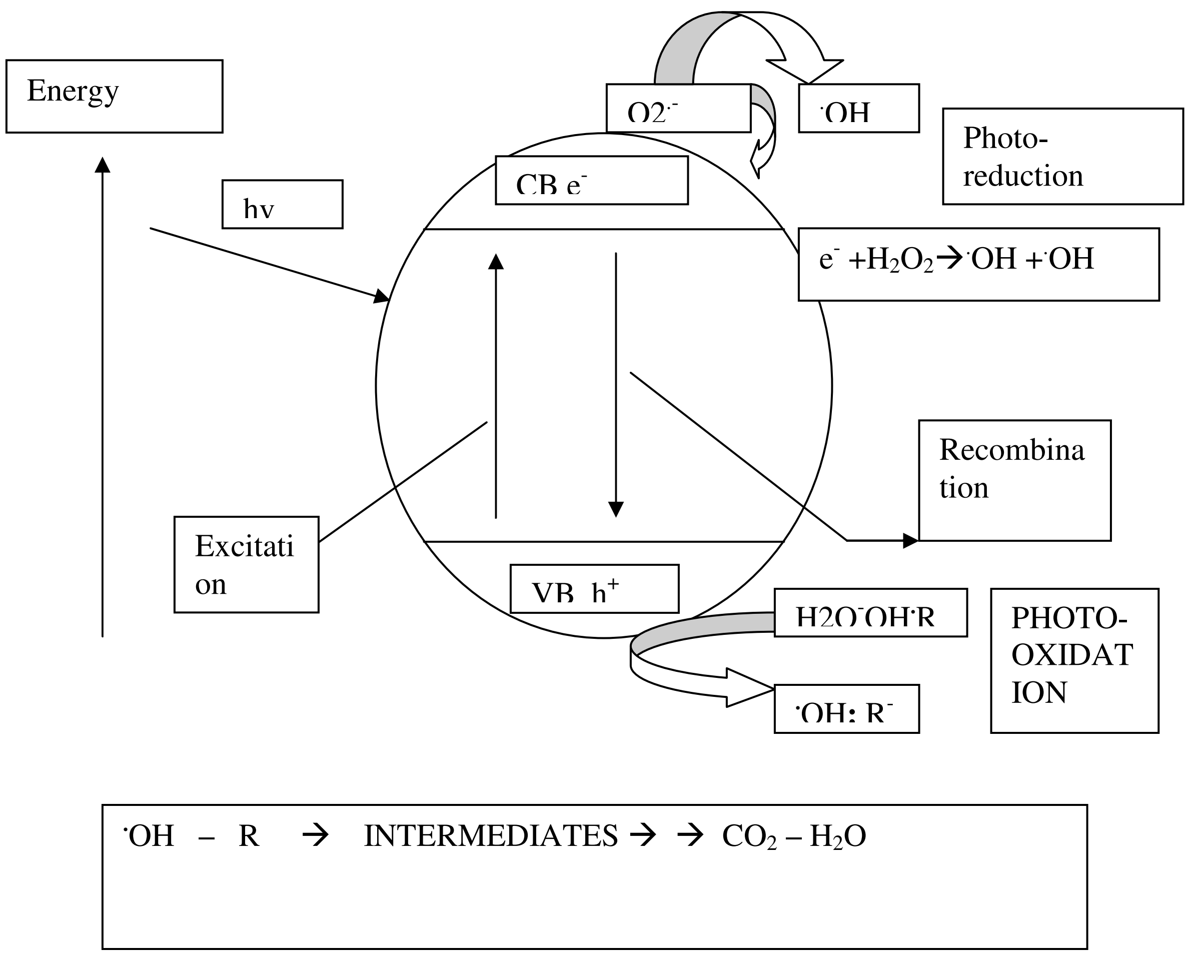
- VB potential must be higher tan material to be degraded.
- Radiation wavelength should be equal or lower than calculated by Planck's equation.
- TiO_2 available in three forms- Anatase (EBg = 3.2 eV), Rutile (EBg = 3.0eV) & Brookite (not used for water treatment.)
- Anatase having higher surface area, surface density of active sites for adsorption.
- Titanium dioxide Degussa P-25 used for environmental applications have anatase

rutile ratio (70:30), surface area 50 m^2 g^{-1}, diameter 21nm.

4.3.4.2 Events taking place on irradiated semiconductor particle **[refer F 4.5] ------**

- On stroked by a particular energy photon electron excitation occurs in valence band.

- Valence band electron jumps to conduction band, creating a hole in the valence band.
- On losing the energy in its way electron may be demoted to conduction band, occupying the hole created before, called recombination.
- Electron now produces $^{\cdot}OH$ and OH- on reaction with H_2O_2.
- Electron may produce $^{\cdot}O_2$- on reaction to O_2 and then $^{\cdot}OH$ and on reaction with H_2O_2.
- Hole produces $^{\cdot}OH$ on reaction to H_2O.



F 4.5 - Showing events taking place on irradiated semiconductor particle

4.4 Applications to water treatment

UV light can be used in several ways. But direct photolysis can occur only when the contamination to be destroyed absorbs incident light efficiently. In the case of UV/ozone and UV/hydrogen peroxide this doesn't happen. But absorption by some sensitizer must initiate the reaction, and limited absorption by the solute or the additive restricts efficiency. In heterogeneous photocatalysis, dispersed solid particles absorb larger fractions of the UV spectrum efficiently and generate chemical oxidants in situ from dissolved oxygen or water. These advantages make heterogeneous photocatalysis a particularly attractive method for environmental detoxification.

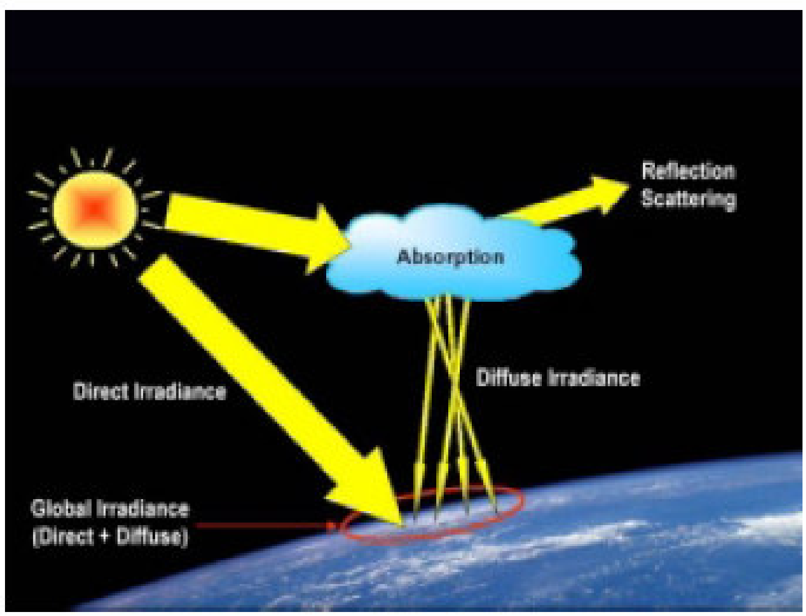
4.5 Perspectives of Solar Field Technology

4.5.1 Solar radiation as source of light

Solar radiation and in particular its ultraviolet component**,** is considered of interest being the existence of ultraviolet radiation the key of some heterogeneous and homogeneous photocatalytic processes, such as TiO_2/UV and H_2O_2/Fe^{2+}/UV-vis or H_2O_2/Fe^{3+}/UV-vis system (photo-Fenton). The use of solar light as source of radiation in the TiO_2/UV- vis system has been studied, taking as reference the recent development of solar technology in water detoxification by means of heterogeneous photocalysis (TiO_2/UV) (Bahnemann *et al.*, 1994; Malato, 1999; Blanco and Malato, 2001). In this sense, this section describes the power of sunlight as source of energy, as well as the basic factors related to the photocatalytic technology and its application. In addition, it outlines the basic principles related to the solar spectrum and especially to the solar UV radiation since this part of the solar spectrum is the most important one for driving chemical processes and the main features of the collectors used for wastewater detoxification.

4.5.2 Solar radiation

Solar radiation is all the energy coming from that huge reactor, the sun, from which the earth receives 1.7×10^{14} kW, meaning 1.5×10^{18} kWh per year, or approximately 28000 times the world energy consumption per year. The wavelength of the radiation beyond the atmosphere ranges between 0.2µm and 50µm. This range is reduced to 0.3 µm and 3.0 µm when reaching the earth surface due to the absorption of part of the radiation by different atmospheric components (e.g., ozone, oxygen, carbon dioxide, aerosols, steam, and clouds). Solar ultraviolet radiation is only a very small part of the total solar spectrum, going between 3.5%and 8%, as demonstrated by measurement, although this percentage may vary for a given location on cloudy and clear days. The percentage of global UV radiation (direct + diffuse) generally increases with respect to the total global radiation when atmospheric transmissivity decreases mainly because of clouds, but also because of aerosols and dust. In fact, the average percentage of UV with respect to total radiation on cloudy days is up to two percent points higher than values on clear days.The solar radiation that reaches the ground level without being absorbed or scattered, is called direct radiation; the radiation, which has been dispersed but reaches the ground level is called diffuse radiation and the addition of both is called global radiation **(See F 4.6).**



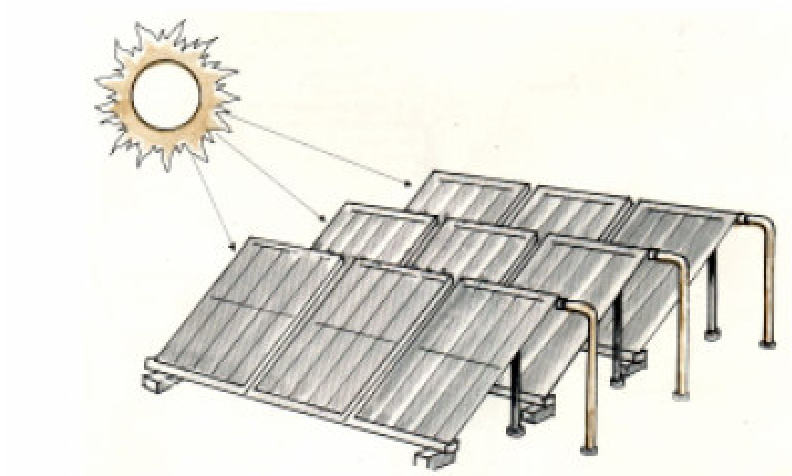
F 4.6 - Showing direct and diffuse radiation.

4.6 Solar collectors

Traditionally, the different solar collector systems have been classified depending on the concentration level attained with them (relationship between the collecting surface and the surface where the final result is produced), which is directly related with the system working temperature. According to this criterion, there are three types of collectors:

I. No concentration or low temperature, up to 150º C
II. Medium concentration or medium temperature, from 150º C to 400º C
III. High concentration and high temperature, over 400º C.

Non-concentrating solar collectors (**F 4.7**) are static, without any solar tracking device. They are usually a flat plate, in many cases aiming to the sun with a determined tilt, depending on the geographic situation. Their main advantage is the reduced cost and, for many applications, the collected radiation is sufficient.

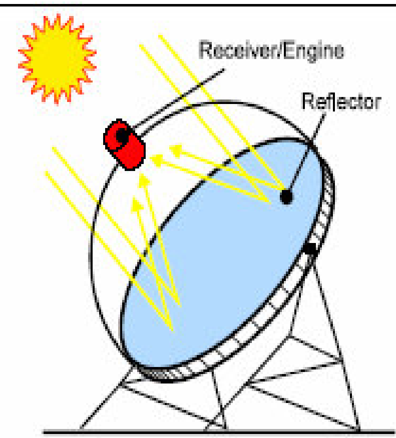


F 4.7 - Showing non-concentrating solar collectors.

Medium concentration solar collectors concentrate the sunlight between 5 and 50 times. Parabolic Trough Collectors (PTC) and collectors with Fresnel lenses are within this group. The first ones have a parabolic reflecting surface which concentrates the radiation on a tubular receiver located in the focus of the parabola.

F 4.8 - Showing medium concentration solar collectors.

High concentration collectors have a focal point instead of a linear one and are based on a paraboloid with solar tracking. Parabolic dishes and solar furnaces are among them Typical concentration ratios are in the range of 100 to 10000 requiring optimal precision elements.



F 4.9 - Showing high concentration collectors.

4.7 Industrial Applications of Solar Radiation

Solar thermal power is one of the main candidates to provide a major share of renewable clean energy needed in the future because:

• Solar radiation is the largest renewable resource on earth. Approximately 1% of the world's desert area utilized by solar thermal power plants would be sufficient to generate the world's entire electricity demand anticipated for the year 2000.

• Solar radiation is more evenly distributed in the Sunbelt of the world than wind or biomass, allowing for more site locations.

• It is among the most cost effective renewable power technologies with power generation costs to be expected in the range of 6 to 15 ct/kWh. And it is the lowest cost solar electricity in the world, promising cost competitiveness with fossil-fuel plants in the future.

• It is a proven and demonstrated technology. Over 100 years of accumulated operating experience, with nine solar thermal power plants of the parabolic trough type feeding over 8 billion kWh of solar-based electricity into the Californian grid, demonstrate the soundness of the concept.

The concentrator captures and concentrates solar radiation, which is then delivered to the receiver. The receiver absorbs the concentrated sunlight, transferring its heat to a working fluid. The transport-storage system passes the fluid from the receiver to the power-conversion system; in some solar-thermal plants a portion of the thermal energy is stored for later use.

One of the most important reactor-design issues is the decision between concentrating or non-concentrating collector systems. Concentrating systems present the advantage of much smaller reactor-tube area, which could mean a shorter circuit in which to confine, control and handle the contaminate water to be treated. If concentrating collector system has to be used, an improving alternative, from both economical and engineering points of view, would be the use of high-quality ultraviolet-light-transmitting reactors. Nevertheless, concentrating reactors have two important disadvantages compared to non- concentrating ones. The first one is that they cannot concentrate (i.e. use) diffuse solar radiation. This fact is irrelevant for solar thermal applications because diffuse radiation is just a small fraction of the total solar radiation. However, this disadvantage becomes important in solar TiO_2-photocatalytic and photo-Fenton detoxification as it uses only the UV fraction of the solar spectrum from which as much as 50 percent can be diffuse, since it is not absorbed by water vapor (Romero et al., 1999). This percentage can be even higher in very humid location or during cloudy or partly cloudy periods. In this sense, efficiency of non-concentrating solar collectors can be noticeably higher, as they can take advantage of both direct and diffuse UV radiation. The second disadvantage of concentrating collectors is their complexity, cost and maintenance requirements. As a consequence of these disadvantages, the present state-of-the art favors the use of non-concentrating reactors for solar photocatalytic applications.

CHAPTER 5

MATERIALS AND METHODS

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

5.0 Materials

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

5.0.1 Synthetic sample

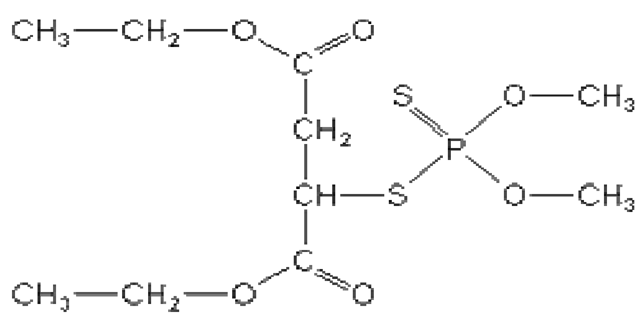
Technical grade pesticide having (purity >90%) of Malathion was collected from the Dhanuka group of pesticide industries. The Dhanuka group of pesticide industries was located on the Joshi road, Karol Bagh in the New Delhi. The sample was given free of cost in the plastic bottles and all the precautions and safety precautions were guided with the help of pamphlet provided with it.

Status: ISO 1750 (published)

IUPAC: diethyl (dimethoxy phospinothioylthio) Succinate.

Formula: $C_{10}H_{19}O_6PS_2$.

Activity: acaricides (organothiophosphates acaricides)
insecticides (aliphatic organothiophosphate insecticides)



F 5.1 - Structure of malathion

5.0.2 Reagents and chemicals used

The photocatalyst was TiO_2 P-25 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, procured form Degussa company, Indian Branch, Bombay with a BET surface area of 50±15 m^2g^{-1} and average particle size of 30nm).Hydrogen peroxide (Ranbaxy laboratories) was used as an oxidant. For COD estimating, COD reagent (containing Silver sulphate and conc. Sulphuric acid) and ferroin indicator were used. For determination of BOD phosphate buffer, calcium chloride, ferric chloride, Magnesium sulfate, Mangneous sulphate, potassium iodide, Sulphuric acid, sodium thiosulphate and starch were used .All chemicals were used as received. In all the experiments distilled water was used.

5.1 Equipment and Instruments

5.1.1 pH meter

The pH of the solution was adjusted with the help of 1N HCl and 1N NaOH and measured using ELICO, India LI 120-pH meter.

5.1.2 Filtration

Samples after the photocatalytic treatments were filtered through injection filters (pore size 0.45um).Whattman's filter paper (No.42) were also used.

5.1.3 Reactors

For the photocatalytic process reactors used were either cylindrical in shape or made of borosil glass, which has a diameter 7.5 inches and is 2 inches in height with a capacity of approximately 1000ml.

5.1.4 COD Digester

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

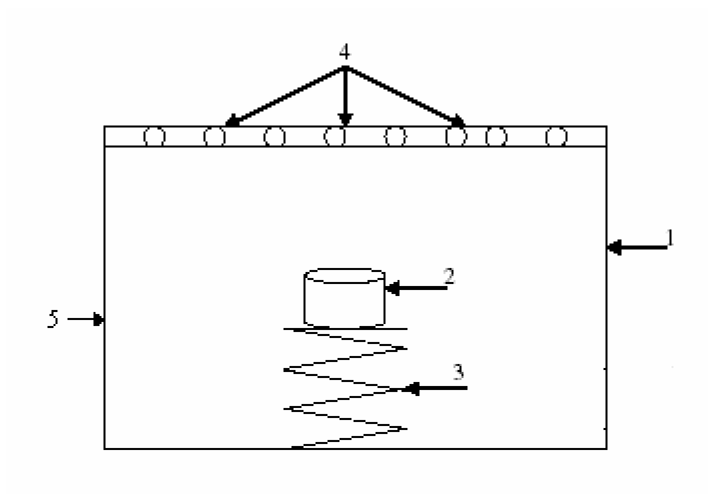
5.1.5 UV-Visible Spectrophotometer

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

F 5.2 - Showing work on the spectrophotometer.

5.3 Shallow pond slurry reactor

A diagrammatic representation of the experimental set up of artificial light irradiated shallow pond batch reactor is shown in Fig. 5.3. UV reactor was rectangular in shape having dimensions of length 4.5m, width 3.0 m and height 3.5 feet and made up of GI sheet. Reactor was mounted with wooden roof. It is equipped with seven 36 W UV tubes (Philips) attached to the roof having wavelength of 365 nm fitted in parallel on the top of the chamber. Small holes are given on the sidewall of the chamber to maintain a constant temperature and for proper circulation of air. The reactor is placed on a lab jack so that required intensity could be attained by adjusting the distance of the reactor from the UV tubes. The UV intensity in the reactor can be varied from 10 to 30 Wm^{-2} corresponding to the average intensity of UV radiation in sunlight. The process is carried out in open atmosphere and oxygen purging is done from time to time. Temperature inside the reactor was maintained by an exhaust fan.



F 5.3 - Schematic diagram of lab scale set up: (1) UV chamber, (2) Reactor, (3) Lab jack, (4) UV lamps, (5) Holes.

5.4 Experimental Procedures

5.4.1 Sample preparation

Pesticide collected from Dhanuka group of pesticide industries was highly concentrated. First of all the survey was done in different regions of Punjab and Haryana (Fatehabad,Sirsa) after that the same concentration i.e. is 5ml/l that is being used by the farmers in the field is taken and accordingly the sample preparation was done in the laboratory. Also to get the values of COD within range, the sample that was prepared as a concentrated sample, was further diluted

5.4.2 Using shallow pond slurry reactor

1. Stock solution of pesticide (Malathion technical grade) was prepared in distilled water for all the experiments.
2. The UV tubes were turned on and allowed to warm up for 20 minutes before the experiment was started as shown in **(F 5.4)**

3. Once the lamps were warmed up, the lab jack (with magnetic stirrer at its top) was raised or lowered until the UV radiometer measured the desired intensity at reactor plane.
4. Then 200 ml of solution was taken in the batch reactor and to it, was added the optimum amount of catalyst.
5. This solution was then irradiated under UV lamp with continuous stirring using a magnetic stirrer in the UV chamber for the required period.
6. An aliquot of 5 ml was taken from the reactor at regular interval of time with the help of a syringe.
7. The catalyst was filtered from the sample by Millipore filter (0.45 µm). These samples were analyzed using UV -Vis spectrophotometer as well as for COD estimation.
8. The pH of the final solution was noted.

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

F 5.4 Experimental UV chamber with glass reactors

5.4.3 Estimation of BOD

BOD was estimated as per standard method No.5210B, page no. 5-4 from STANDARD METHODS for the examination of water and wastewater, 1987(17th edition).

5.4.4 Estimation of COD

COD was estimated as per the standard method No. 5220 C, page no. 5-14 from STANDARD METHODS for the examination of water and wastewater, 1989(17th edition). For all the samples 50 times dilution was made so as to get COD within range. Samples were digested in COD block digester as well as semi-automatic autoclave.

CHAPTER – 6

RESULTS AND DISCUSSIONS

6.0 Pesticide characteristics

Technical grade (99%) pure form of the malathion pesticide was taken from Dhanuka group of industries The Dhanuka group of pesticide industries was located on the Joshi road, Karol Bagh in the New Delhi. The pesticide sample of technical grade was taken and analyzed for its various parameters. The values of the various parameters are shown in **(T 6.1)** before treatment .and their degradation studied by using different things like different catalyst concentration, different pH, different H_2O_2 concentration and than after optimizing the different parameters the degradation of the pesticide in the UV-visible spectrophotometer at different time intervals were studied both by the COD reduction as well as by the absorption.

Parameter	Value
pH of pesticide	3.5 (Acidic)
COD of sample	11200 mg/L
Absorb. (max)	215 (nm)

T 6.1 - Showing characteristics of raw malathion technical grade pesticide from Dhanuka industries.

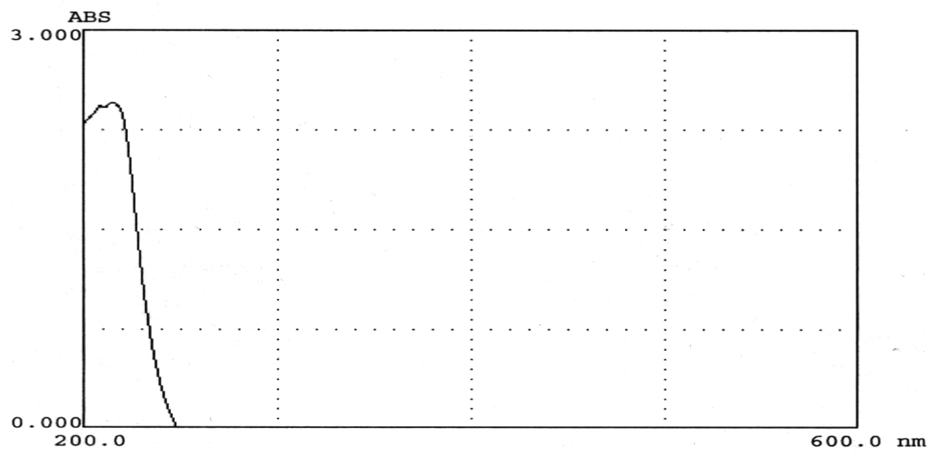
Above listed parameters reveals that the technical grade of the Malathion pesticide used in the fields by the farmers was highly toxic product and cause a number of pollution problems in the environment. So to reduce the adverse affect of this pesticide on the environment and human health before releasing into the environment require proper treatment before its disposal satisfying the safe prescribed limits from environment point of view.

6.1 Absorption spectra of raw pesticide sample

As shown in the **(F 6.1)** below the absorption spectra of the raw pesticide sample shows the peak in the UV and visible region and maximum absorbance (2.448) was observed at wavelength 215 (nm), which indicates that the pesticide is highly toxic and needs the degradation for the complete mineralization of the toxic compounds and to overcome the toxic
effect

U-2800 Spectrophotometer

Serial Number:	5920070
ROM Version:	11
Sample Name:	B B
Date:	04/04/08 11:34
Operator:	



Wavelength Scan

Data Mode:	ABS
Start WL(nm):	600.0
Stop WL(nm):	200.0
Scan Speed(nm/min):	200
Sample Interval(nm):	0.5
Baseline:	None
Response:	Medium
Slit Width(nm):	1.5
Path Length(mm):	10.0
Lamp Change Mode:	Auto
Lamp Change WL(nm):	340.0

Peak

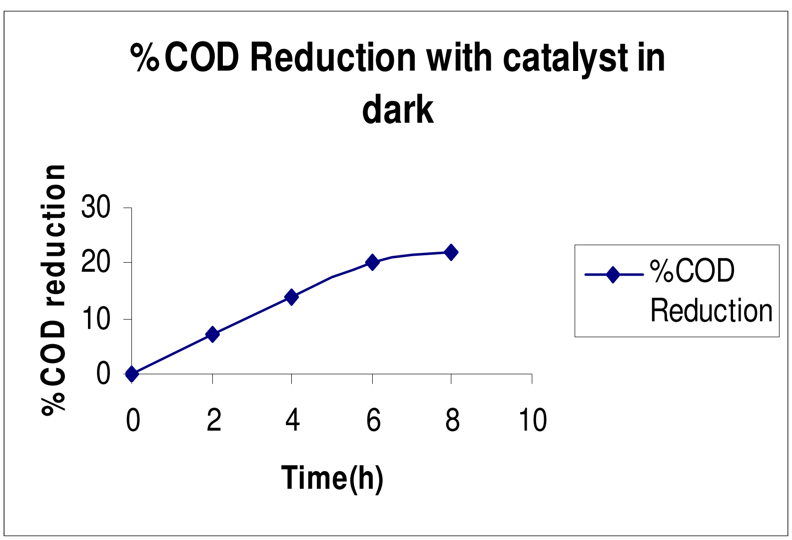
ID	WL(nm)	ABS	ID	WL(nm)	ABS	ID	WL(nm)	ABS
1	600.0	-0.070	2	584.5	-0.245	3	215.0	2.448
4	209.0	2.423						

F 6.1 - Showing absorption spectra for the raw pesticide sample.

6.2 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. The addition of the catalyst concentration in the dark showed a very little degradation. The degradation rate became constant after some time as confirmed by the constant COD values because of the monolayer formation on the catalyst surface. As soon as the catalyst was added, pesticide from solution adsorbed on the surface, thus lead to decrease in COD values in the solution. But after the formation of monolayer on the catalyst surface, reduction in COD values became constant. Thus results observed from adsorption experiment confirmed that decrease in COD was due to adsorption i.e. no degradation of the pesticide was confirmed. So for the complete degradation of the technical grade pesticide some alternative method should be used.

In this study, the pesticide sample of 200ml was placed for many hours without the addition of the catalyst, neither pH nor addition was done in this process after one week period the sample was tested for the COD reduction process and 10-20% COD reduction of the pesticide sample was observed **(F. 6.2)**.



F 6.2 - Showing COD reduction with catalyst in dark.

6.3 Photolysis Process

In literature there is a number of numbers of reports cited for pesticides degradation by photolysis. To confirm the results, UV degradation of pesticide was done to confirm that pesticide in our study was not degraded by UV-light completely so for the complete degradation of the pesticide photocatalytic treatment would be best option. The basis of photolysis is the photo-excitation of a solid, as a result of the absorption of electromagnetic radiation, often, but not exclusively, in the near UV spectrum. Under near UV irradiation a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation respectively.

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

$$h^+ + A^- \longrightarrow {}^{\cdot}A$$

$$h^+ + OH.^- \longrightarrow {}^{\cdot}OH$$

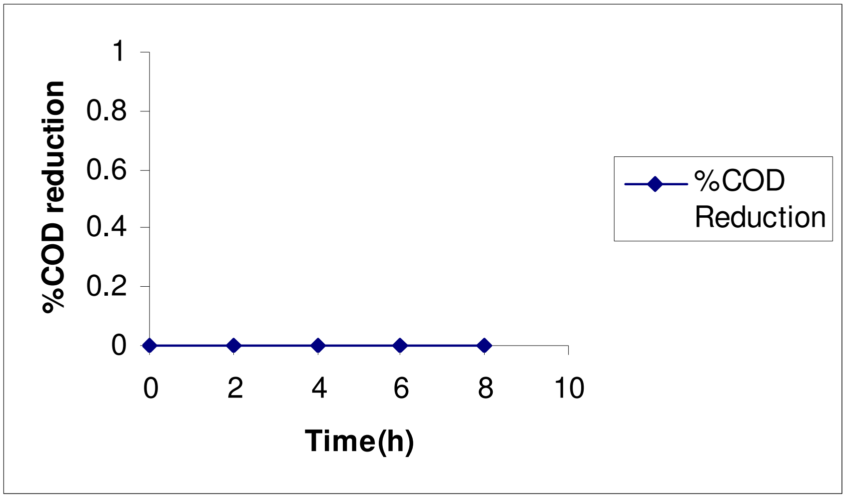
$${}^{\cdot}OH + RH \longrightarrow {}^{\cdot}RHOH$$

$${}^{\cdot}OH + RH \longrightarrow {}^{\cdot}R + H_2O$$

$$h^+ + RH \longrightarrow {}^{\cdot}RH^+$$

Holes may possess an extremely positive potential and should thus be able to oxidize almost all chemicals. Even the one-electron oxidation of water resulting in the formation of hydroxyl radicals should be energetically feasible. **(F 6.3**) Showing COD reduction in presence of UV light.

$$H_2O + h^+ \longrightarrow {}^{\cdot}OH + H^+$$



F 6.3 - Showing COD reduction without catalyst in UV.

6.4 Photocatalytic treatment

After characterization of the waste sample, its photocatalytic treatment was done. Photocatalytic treatment depends upon the following factors:

1. Catalyst concentration
2. Operating pH
3. Oxidant addition

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

6.4.1 Radiation conditions during experimental days

During the experimental, the intensity was measured with the help of UV radiometer. The kept intensity ranges from 25-28 W/m^2.The intensity range was kept from25-28 W/m^2 is just to match intensity of UV radiations that we are getting from sunlight during the experimental months.

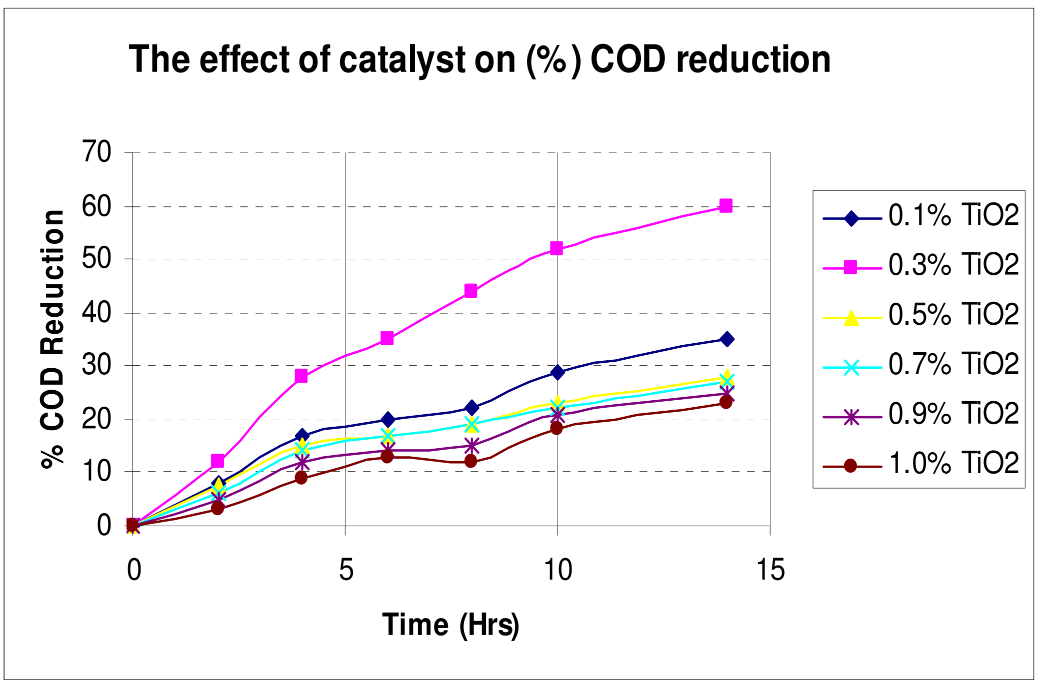
6.4.2 Catalyst concentration

Photocatalyst (TiO_2) concentration was varied from 1.0 g/l to 10 g/l (i.e. 0.1% to 1.0%) during reactions for studying the pesticide degradation rate at different concentrations. It was observed that degradation rate of pesticide increases with increased catalyst concentration and becomes constant above a certain level as shown in (**F 6.4)** and after one particular optimize dose the degradation rate of the pesticide starts to decrease. The reasons for this decrease in degradation rate are:

(i) Aggregation of TiO_2 particles at high concentrations causing a decrease in the number of surface active sites and

(ii) Decrease in opacity and light scattering of TiO_2 particles at high concentration.

An amount of 0.3% catalyst concentration of 200ml sample has been taken for the subsequent experiments for studying the effect of oxidant addition and pH of the solution.

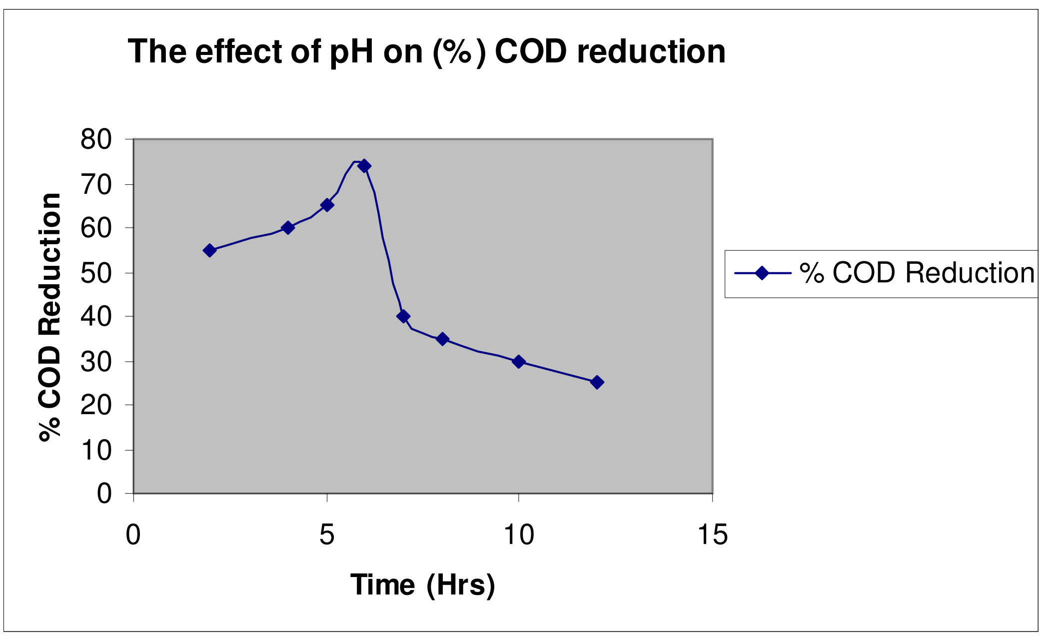


F 6.4 – Showing effect of catalyst concentration on the COD reduction.

From the graph shown above, we observe that the COD continuously decreases on increasing the catalyst concentration ranging from 0.1%-1%. But the optimum dose of the catalyst at which the highest COD reduction was observed was 0.3%concentration of the catalyst, that is the optimum dose of the catalyst after that COD reduction goes on decreasing as shown in the graph. An optimum of catalyst concentration has to be taken when the decrease in COD level are to be within acceptable limits.

6.4.3 Effect of operating pH

pH may be defined as the negative logarithm of hydrogen ion concentration. The pH of anything is set on a scale of from 1 to 14. The pH plays an important role both in the characteristics of pesticide and generation of hydroxyl radicals. With increased pH the degradation also increasing but up to certain level the increased degradation of pesticide was observed as shown in the **(F 6.5)** after that decrease in the degradation rate starts.



F 6.5 – Showing effect of pH on the % degradation of the pesticide solution.

According to literature reports, the pH of the solution significantly affects TiO_2 activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valence bands. In our experiments, maximum degradation of the pesticide was observed at pH near 6, so optimum pH should be at 6 because maximum degradation was achieved at this pH, beyond this pH the degradation rate of pesticide decreased as shown above.

6.4.4 Effect of Oxidant addition

Hydrogen peroxide can enhance the photocatalytic activity by providing an additional oxidant source and by reducing the rate of recombination between the holes and electrons in the activated titanium dioxide particles.

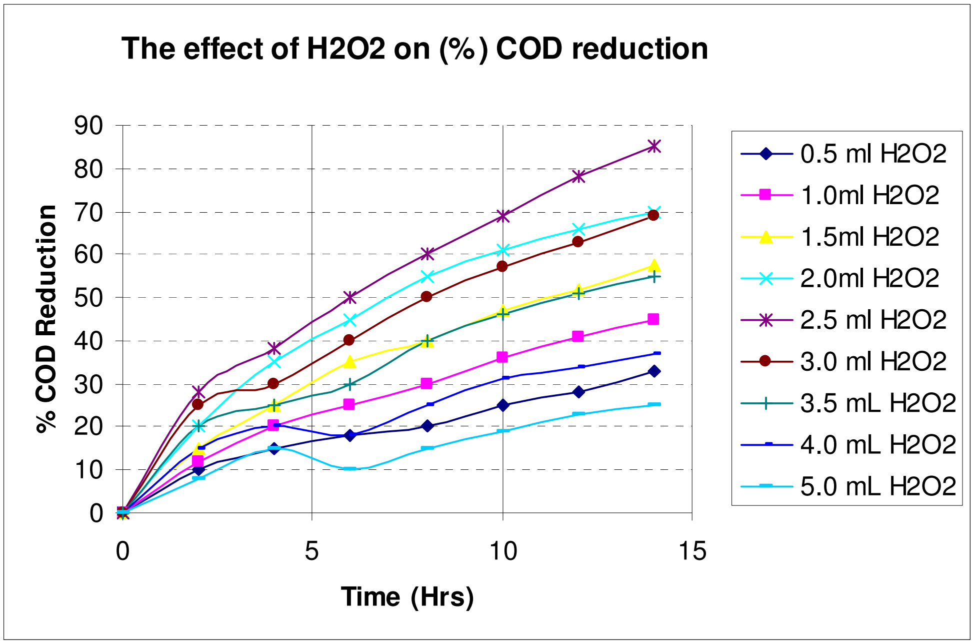
$$\mathbf{TiO_2\,(e^-) + H_2O_2 \;\text{---------------->}\; TiO_2 + OH^- + OH^{\cdot}} \qquad \textbf{(a)}$$

The objective of the experiment is to measure the effect of added hydrogen peroxide on the destruction of organics. Hydrogen peroxide having two main functions in the process of photocatalytic degradation. It accepts a photo generated electron from a conduction band and thus promotes the charge separation, and it also forms OH radical, according to Eq. (a). At high concentration of H_2O_2, it acts as a scavenger as shown in the following equations:

$$\mathbf{H_2O_2 + OH^{\cdot} \;\text{---------------->}\; HO_2^{\cdot} + H_2O}$$

$$\mathbf{HO_2^{\cdot} + OH \;\text{---------------->}\; H_2O + O_2}$$

The experiments conducted by varying the hydrogen peroxide concentration from 1.0 to 5 ml per 200ml of the pesticide sample. The best results were obtained when oxidant addition came out to be 2.5 ml/200ml of pesticide sample and have been taken as the optimum amount required for maximum effective degradation of toxic pollutants.**(F 6.6)** shown below shows that 2.5ml is the optimum dose of the oxidant H_2O_2 at which maximum pesticide degradation was observed.



F 6.6 - Showing effect of oxidant addition (H_2O_2) on the COD reduction.

6.5 Pesticide characteristics after treatment in the UV- reactor

Pesticide characteristics were determined after photocatalytic treatment process under the optimized conditions i.e. at TiO_2 of 0.3% of 200ml, 2.5 ml of oxidant and at operating pH of 6 (**T 6.2**) – Shows the parameters analyzed after the treatment in the UV-reactor and their values shows the major reduction of the technical grade pesticide.

Property	**Value**
pH of pesticide	2.0 (Acidic)
COD of sample	<4000 mg/l
Absorb. (max)	< 0.5(nm)

T 6.2 – Showing characteristics of the Malathion technical grade pesticide after Treatment

6.6 Comparison studies of degradation of pesticide under UV light and solar radiations using slurry reactor

Results obtained from the degradation studies of pesticide using artificial UV light source were compared with treatment under natural solar conditions **(F 6.7)**. After optimizing the conditions with UV source i.e. 0.3% TiO_2, 6 pH, 2.5 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.

It was observed **(F 6.8)** that the degradation of the pesticide was appox. 80% after 7-8 hrs of treatment under sunlight as compared to 70% in artificial UV conditions in the same duration of time and under same intensity.

F 6.7 - Showing solar photocatalytic treatment

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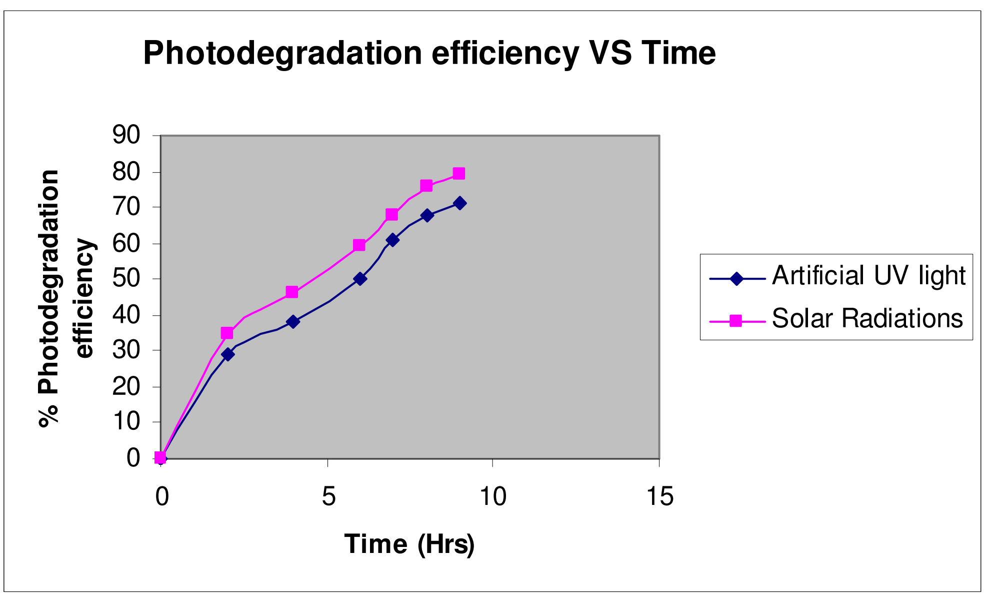
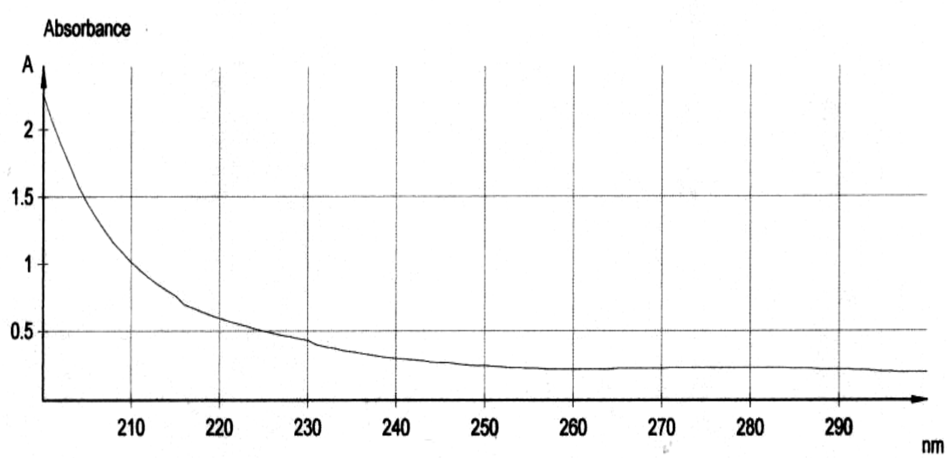


F 6.8 - Showing (%) photo degradation efficiency Vs. Time

6.7 Absorption spectra after photocatalytic treatment

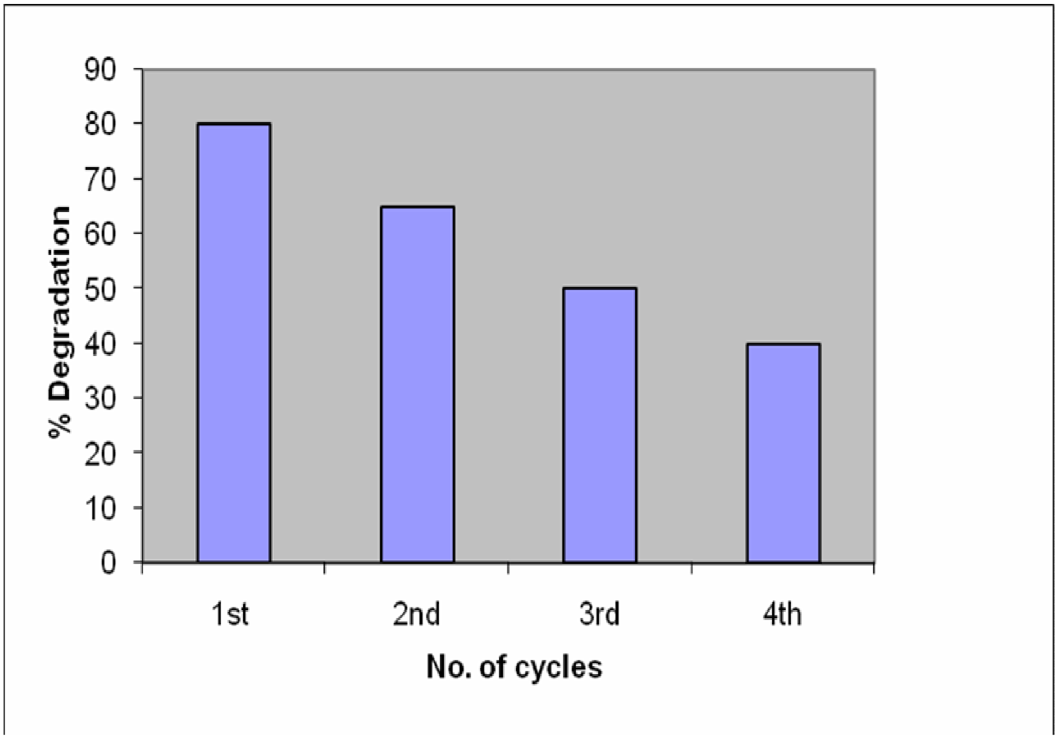
The spectra shown below in the **(F 6.9)** is of the technical grade of the pesticide malathion from this spectra it reveals that after treating the sample with optimized conditions in the UV-reactor for more than 12 hours time period, the toxic and harmful compounds breakdown to the harmless ones. As 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.



F 6.9 - Showing absorption spectra for pesticide after photocatalytic treatment.

6.7 Catalyst Recycling

During photocatalytic treatment catalyst recycling is one of the major challenges towards the large scale applications. Catalyst fouling and loss of catalyst during filtration is the major cause behind the drop in the efficiency of the catalyst. During our studies, the catalyst was effectively recycled for at least four times but with the reduction in the



F 6.10 – Showing catalyst (TiO_2) recycling.

degradation efficiency. After the each run, the catalyst was filtered using wattmann filter paper no.22 and catalyst was activated at 105^0C. The catalyst lifetime is an important parameter for industrial applications of photocatalytic and also to reduce the cost of the catalyst significantly.

CONCLUSION AND RECOMMENDATIONS

Conclusions

Photocatalytic process can efficiently degrade the pesticides using artificial UV-light or sunlight radiation sources. The observations, clearly demonstrates the importance of choosing optimum degradation parameters to obtain high degradation rates which is most essential for any practical applications of photocatalytic oxidation processes. In this work, the photocatalytic oxidation of pesticide Malathion has been studied using TiO_2 as a photocatalyst. Studies reveal that photocatalytic oxidation of the pesticide in a shallow pond reactor can be efficiently done. The optimum conditions for photo degradation of pesticides are 0.3% catalyst concentration, 2.5ml H_2O_2 and 6.0 pH.

Results can be implemented with certain modifications at large level, to efficiently remove pesticide from water/wastewaters which are not conveniently removed by conventional treatment. Large shallow pond reactors can be made and incorporated 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 photocatalytic degradation processes or rates are highly dependent on the molecular structure of the solute. Same was experienced during our studies while working on sulfosulfuron. Nearly a month was spent to degrade the pesticide using photocatalytic processes but somehow we did not succeed in much degradation of above said pesticide. This might be due to the fact that photocatalytic degradation rates depend upon the molecular structure of the pesticides.

Recommendations

Much work is needed to develop, more accurate method for modeling the kinetics of water or wastewater containing pesticides. Advanced oxidation processes for water and wastewater 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 n advanced oxidation processes there is a need of the future research that must lead to the reduction of treatment cost. Future research must also investigate the effectiveness of these technologies in combination with other cost-effective treatments such as biological treatment for the 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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