FIXED BED PHOTOCATALYSIS FOR THE DEGRADATION OF 2-CHLORO 4-NITROPHENOL USING SOLAR IRRADIATION

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By

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July 2012

DECLARATION

I hereby declare that the work embodied in dissertation entitled, "**Fixed bed photocatalysis for the degradation of 2-Chloro 4-Nitrophenol using solar irradiation",** is original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

Jayant Srivastava

CERTIFICATE

This is to certify that the dissertation entitled, "Fixed bed photocatalysis for the degradation of 2-Chloro 4-Nitrophenol using solar irradiation", is an authentic work carried out by Jayant Srivastava student of M.Tech. (Environment Science and Tech.) Thapar University, Patiala, during the year 2011-2012, in partial fulfilments for the award of the Degree of Master of Technology and that the dissertation has not formed the basis for the award previously of any degree, associateship, fellowship or any other similar title to any other university or institute.

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Abstract

Phenol and phenolic compounds occur as waste from various industries like Oil refining, petrochemical, coal mining, lignite transformation etc. and result in bioaccumulation. Water from natural sources is mainly polluted due to chemicals present in the wastewater let out from industries of various domains. High COD, opacity, high alkalinity/acidity, high total solids and high BOD are the characteristic of industrial wastewater. This creates an imbalance in the ecosystem and hence treatment of such wastewaters is needed. 2 chloro 4 nitro phenol (2-C 4-NP) is one among the mostly used phenolic compound. It is used as an intermediate in wood preservative, in the medical treatment of obesity, and also in a pesticide. An effective and economic treatment for eliminating phenolics in water has been in urgent demand. One method to remove 2-C 4-NP from the wastewater is fixed bed photocatalysis.

Photocatalysis is a technique that uses solar radiation and a photocatalyst, the photon energy from sun is used for generating hydroxyl radicals formed as a result of oxidation of catalyst that remove organic matter in wastewater.

TiO_2 is one of the most popular and promising materials, because of its stability under harsh conditions, commercial availability, different allotropic forms with high photo-activity, possibility of coating as a thin film on solid support, ease of preparation in the laboratory etc. Its absorption spectrum overlaps with the solar spectrum and hence opens up the possibility of using solar energy as the source of irradiation. To eliminate the need of filter during post-treatment removal using suspended photocatalyst, researchers tested various catalyst supports.

The scope of the study is to see the heterogeneous photocatalytic degradation of 2-C 4-NP in TiO_2 fixed bed reactor. For the process optimization like pH, Oxidant dose, initial concentration suspension mode photocatalysis. For the immobilization of catalyst three different supports (cemented beads, glass sheet and sodium alginate balls) are used. The degradation studies in slurry form are investigated using TiO_2 Degussa photocatalysts under UV illumination. The study includes dark adsorption, UV light treatment along with variation in different parameters like pH, amount of photocatalyst, effect of H_2O_2 concentration.

Degradation observed was 89%, 70%, 65% and 60% under suspension solar-photocatalytic, glass-plate solar reactor, coated cemented beads and immobilized sodium alginate ball; respectively at optimized conditions i.e. 4.5 pH, catalyst concentration of 1 g/l and oxidant

dose of 7.5mM/200ml. The dip and coating method was used for the catalyst immobilization on the glass and cemented beads, whereas in other case, physical entrapment of the catalyst slurry in the gel was used. Approximately 95% reduction in COD confirms the mineralization of the compound under study.

Result shows that fixed bed photocatalysis would be more efficient and economical as filtering as well as recovery of the catalyst can be avoided. The application of solar powered photocatalytic reactors to treat waste water from different industries holds promise for regions receiving strong sunlight throughout the year, such as India.

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INTRODUCTION

1.1 Overview:

About three-fourth of the earth's surface is occupied by oceans which contain about 97.5 % of the earth's water in strongly saline condition. The rest 2.5% is fresh water, and all of this is not available for direct human use. Most of the fresh water is frozen as polar or glacial ice (1.97%). Remaining fresh water occurs as ground water (0.5%) and water in lakes and rivers (0.02%), soil (0.01%) and atmosphere (0.0001%). Thus, only a small fraction of fresh water is available for human consumption.

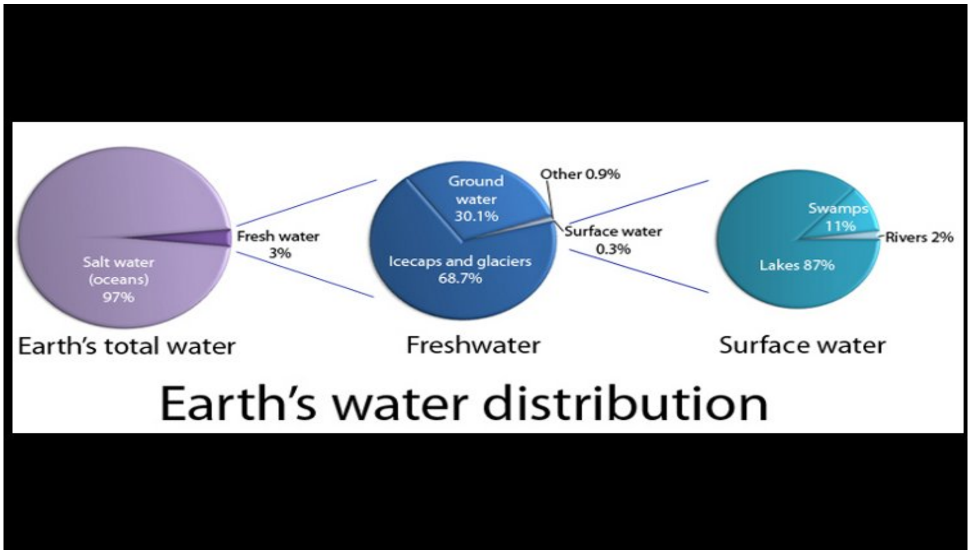


Figure1.1: Earth's water distribution

1.2 Water pollution:

Water pollution means the presence of any foreign substance (organic, inorganic, radiological and biological) in water, which tends to degrade its quality so as to constitute a hazard or impair the usefulness of the water.

Sources of Water Pollution

On the basis of their origin, the sources of water pollutants can be broadly categorized into Point sources, where the effluent discharge occurs at a specific site; Non-point sources, where inflow of pollutants occurs over a large area (figure 1.2).

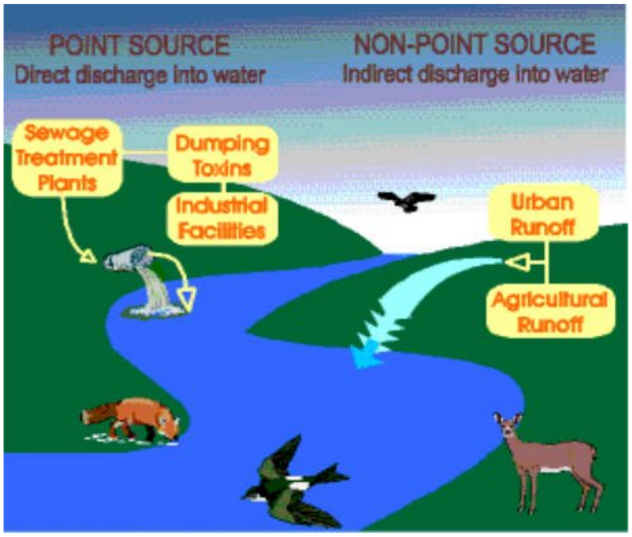


Figure1.2: sources of water pollution

The pollutants from industrial discharge and sewage besides finding their way to surface water reservoirs and rivers are also percolating into ground to pollute ground water sources. There are many types of industrial wastewater based on different industries and the contaminants; each sector produces its own particular combination of pollutants. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produce.

1.3 Health Impacts:

Pollutants in drinking water ultimately reach humans and are known to cause various health problems Domestic sewage contains pathogens like virus, bacteria, parasitic protozoa and worms. Contaminated water, therefore, can carry the germs of water-borne diseases like jaundice, cholera, typhoid, amoebiasis, etc. Such contamination may make the water unfit for drinking, bathing, and swimming and even for irrigation.

Heavy metal contamination of water can cause serious health problems. Mercury poisoning (Minamata disease) due to consumption of fish captured from Hg contaminated Minamata Bay in Japan was detected in 1952. Cadmium pollution can cause itai-itai disease (ouch-ouch disease, a painful disease of bones and joints) and cancer of liver and lung. The important classes of this water pollutant are organic, inorganic, heavy metals; originated from different domestic and industrial process.

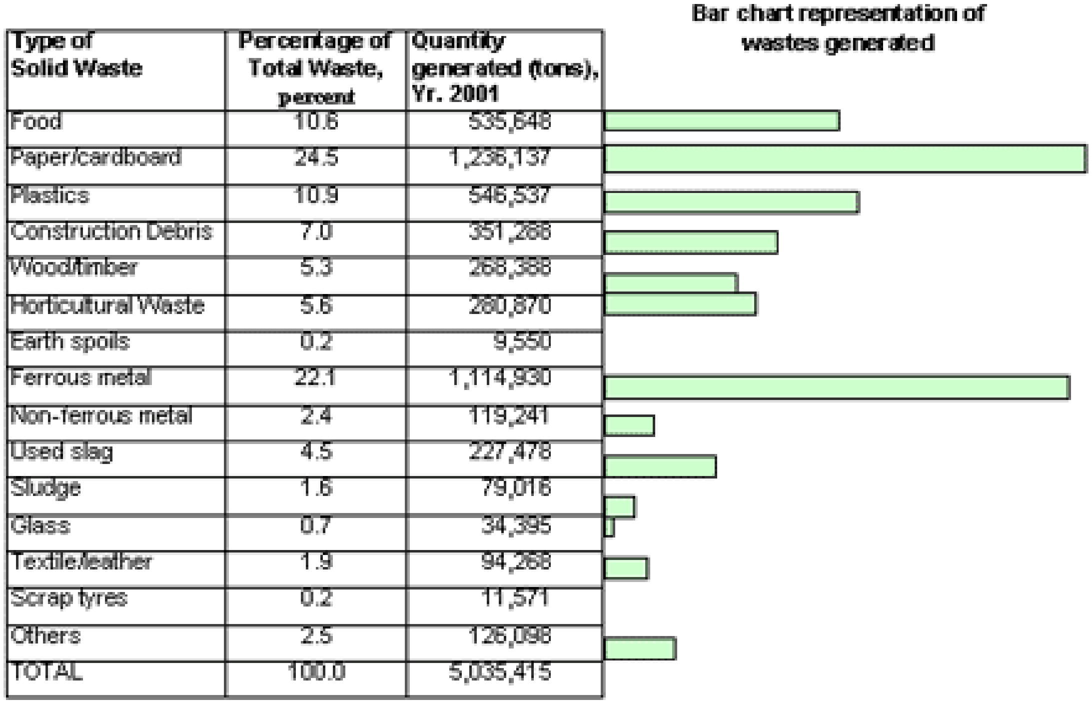
1.3.1 Domestic Waste:

Liquid wastes from domestic activities such as kitchen, toilet and other household wastewater are, in most cases, discharged directly into a river or into a large water body nearby. Many rivers in India, including the river Ganga, are polluted by indiscriminate discharge of wastewater. The famous Dal Lake in Kashmir is also heavily polluted by domestic sewage. Sewage creates two serious environmental problems in water, enrichment and oxygen demand. Enrichment is fertilization of water body by high levels of plant nutrients such as nitrogen and phosphorus. Excess input of nutrients occurs from detergent residues (e.g. phosphates) and organic remains (e.g. nitrates). Domestic effluents mostly carry organic wastes, which are biodegradable and require oxygen. High levels of sewage consume most of the dissolved oxygen leaving little for other aquatic organisms. At extremely low oxygen levels, fishes begin to die off.

1.3.2 Industrial Waste:

Both small-scale and large industrial activities produce wastewater contaminated by a variety of organic pollutants. Almost all the rivers of India, at least in certain stretches, are heavily polluted by the discharge of industrial wastewater. Most components of industrial effluents are toxic to ecological systems even at low concentrations, and many are non-biodegradable. A large number of inorganic chemicals pollute surface water from sources such as industrial plants, mines, oil drilling, and municipal storm water. Mercury is one important inorganic chemicals causing long term impact on kidney function and nervous system. Acid drainage from mines containing high levels of heavy metals is another example of inorganic chemicals in water bodies. (Singh, Y.K. 2006)

In India, water pollution due to industrial wastes and sewage has been assuming menacing proportions. Large lakes and large stretches of most of the rivers in India have water which is unsafe for drinking purpose. Survey of industrialized zones show that even ground water has become unfit for drinking due to high concentration of toxic metals and chemicals along with bacteriological contamination.



Type of Solid Waste	Percentage of Total Waste, percent	Quantity generated (tons), Yr. 2001
Food	10.6	535,648
Paper/cardboard	24.5	1,236,137
Plastics	10.9	546,537
Construction Debris	7.0	351,268
Wood/timber	5.3	268,388
Horticultural Waste	5.6	280,870
Earth spoils	0.2	9,550
Ferrous metal	22.1	1,114,930
Non-ferrous metal	2.4	119,241
Used slag	4.5	227,478
Sludge	1.6	79,016
Glass	0.7	34,395
Textile/leather	1.9	94,268
Scrap tyres	0.2	11,571
Others	2.5	126,098
TOTAL	100.0	5,035,415

Figure1.3: waste generated from industries (source: UNEP[1])

1.4 Waste water treatment process:

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

The use of conventional water and wastewater treatment processes become increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources. (Zhou H and Smith D.W., 2001)

The major drawback of conventional methods is not able to treat toxic, non biodegradable organic pollutants so to meet the challenge of keeping progress in wastewater pollution abatement ahead of population growth, changes in industrial processes and technological developments, advance oxidation techniques have emerged in the past few years, in particularly for industrial waste water.

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[1] United Nation of Environment Protection

1.5 Need of advance treatment:

The use of conventional water and wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources. The advanced oxidation processes (AOPs), hold great promise to provide alternatives for better protection of public health and the environment. (Zhou H. and Smith D.W., 2001)

Advanced oxidation processes (AOPs) (Fig.1.4) have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical (·OH), as the primary oxidant (Glaze 1987).

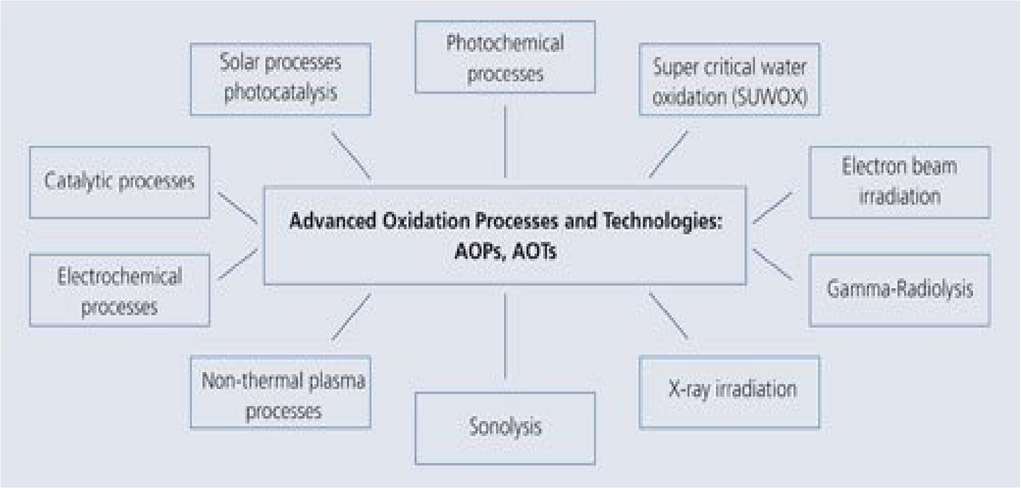

Figure1.4: Classification of AOP's (source: FIIEB[2])

Recently, considerably interest has been shown by all over the world in the application of solar photocatalysis to improve the performance of photocatalytic degradation of organic and inorganic contaminants in aqueous streams. So, research is focusing more and more on those AOPs which can be driven by solar irradiation.

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[2] Fraunhofer Institute for Interfacial Engineering and Biotechnology

CHAPTER 2

PHARMACEUTICAL AND PESTICIDAL WASTE WATER

2.1 Overview of Pharmaceutical industry:

The pharmaceutical industry manufactures biological products, medicinal chemicals, botanical products, and the pharmaceutical products. The industry is characterized by a diversity of products, processes, plant sizes, as well as wastewater quantity and quality. In fact, the pharmaceutical industry represents a range of industries with operations and processes as diverse as its products. Hence, it is almost impossible to describe a “typical” pharmaceutical effluent because of such diversity. Industrialization in the last few decades has given rise to the discharge of liquid, solid, and gaseous emissions into natural systems and consequent degradation of the environment **(**Mehta G. et al., 1995**).** The most frequently detected compounds were basically of pharmaceutical origin, that is, coprostanol (fecal steroid), cholesterol (plant and animal steroids), *N*,*N*-diethyltoluamide (insect repellant), caffeine (stimulant), and triclosan (antimicrobial disinfectant), and so on **(**Kolpin D.W.et al., 2002)**.**

2.2 Process description and waste characteristics:

Based on the processes involved in manufacturing, pharmaceutical industries can be subdivided into the following five major subcategories:

1. Fermentation plants;
2. Synthesized organic chemicals plants;
3. Fermentation/synthesized organic chemicals plants (generally moderate to large plants);
4. Biological production plants (production of vaccines-antitoxins);
5. Drug mixing, formulation, and preparation plants (tablets, capsules, solutions, etc.).

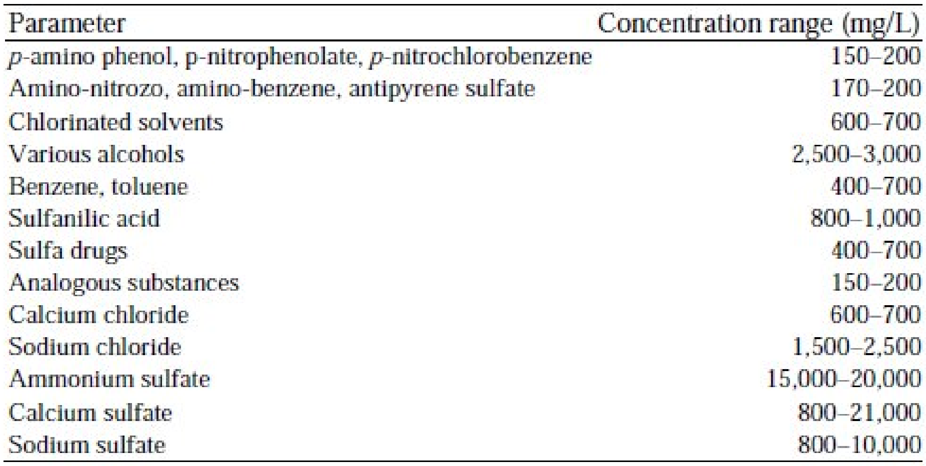
Pharmaceutical waste is one of the major complex and toxic industrial wastes **(**Seif H.A.A.et al., 1992)**.** As mentioned earlier, the pharmaceutical industry employs various processes and a wide variety of raw materials to produce an array of final products needed to fulfil national demands. As a result, a number of waste streams with different characteristics and volume are generated, which vary by plant, time, and even season, in order to fulfil the demands of some specific drugs. It has been reported that because of the seasonal use of many products, production within a given pharmaceutical plant often varies throughout the year, which changes the characteristics of wastewater (Table2. 1) by season **(**Andersen D.R. 1980)**.** Hence, it is difficult to generalize the characteristics of the effluent discharged from these industries.

Table2. 1 Characteristics of Alkaline Waste Stream of a Synthetic Drug Plant at Hyderabad

Ranges (max. to min.)	Parameters from Ref. [Deshmukh S.B et al., 1984]	From Ref. [Murthy Y.S et al., 1984]
Flow (m3/day)	1,400–1,920 (1,710)	1,710
pH	4.1–7.5	2.3–11.2
Total alkalinity as CaCO3	1,279–2,140	624–5630
Total solids	1.29–2.55%	1 1825–23265 mg/L
Total volatile solids	13.1 −32.6% of TS	1,457–2,389 mg/L
Total nitrogen (mg/L)	284–1, 036 (TKN)	266–669
Total phosphorus (mg/L)	14–42	10–64.8
BOD5 at 20°C (mg/L)	2,874–4,300	2,980–3,780
COD (mg/L)	5,426–7,848	5,480–7,465
BOD: COD	—	0.506–0.587
BOD: N:P	—	100:(8.9–17.7):(0.265–1.82)
Suspended solids (mg/L)	—	11–126
Chlorides as Cl− (mg/L)	—	2,900–4,500

Such wastewater has bad colour and high (or low) pH value, and it needs a strong pre-treatment method, followed by a biological treatment process with a long reaction time. In many cases, these effluents contain little or no biodegradable organic matters and the pollutant loads in terms of biological oxygen demand (BOD) may be negligible hence higher chemical oxygen demand (COD) than BOD. (Madukasi et al., 2009)

Table 2.2 Characteristics of Untreated Synthetic Drug Waste



Parameter	Concentration range (mg/L)
p-amino phenol, p-nitrophenolate, *p*-nitrochlorobenzene	150–200
Amino-nitrozo, amino-benzene, antipyrene sulfate	170–200
Chlorinated solvents	600–700
Various alcohols	2,500–3,000
Benzene, toluene	400–700
Sulfanilic acid	800–1,000
Sulfa drugs	400–700
Analogous substances	150–200
Calcium chloride	600–700
Sodium chloride	1,500–2,500
Ammonium sulfate	15,000–20,000
Calcium sulfate	800–21,000
Sodium sulfate	800–10,000

The complexity and multi component nature (Table 2.2) of the waste warrants effective treatment strategies for meeting the specific discharge guidelines of regulatory agencies and hence there is a need of investigating newer treatment strategies for the same.

2.3 Occurrence and fate of pharmaceuticals in environment

Pharmaceuticals are excreted by humans, as a parent compound or metabolite, with urine (mainly) and faeces. Combined with other components of sewage they enter a sewage treatment plant (STP) where they do not get removed to a satisfactory degree so finally they end up in the environment. The medical compounds detected in the environment (water, soil) have recently deserved much attention. As having specific properties they may provoke effects to the aquatic and terrestrial ecosystems even at very low concentrations. They also possess several common features like e.g. polarity or persistence that implicate poor removal and bioaccumulation. In addition, a number of polar pharmaceutical compounds and metabolites, such as diclofenac, carbamazepine, sulfamethoxazole, and amidotrizoic acid, have been detected in groundwater samples at concentrations up to 1mg/l. There are several possible sources and routes for the occurrence of pharmaceutical compounds in the aquatic environment as shown in **Figure-2.1.**

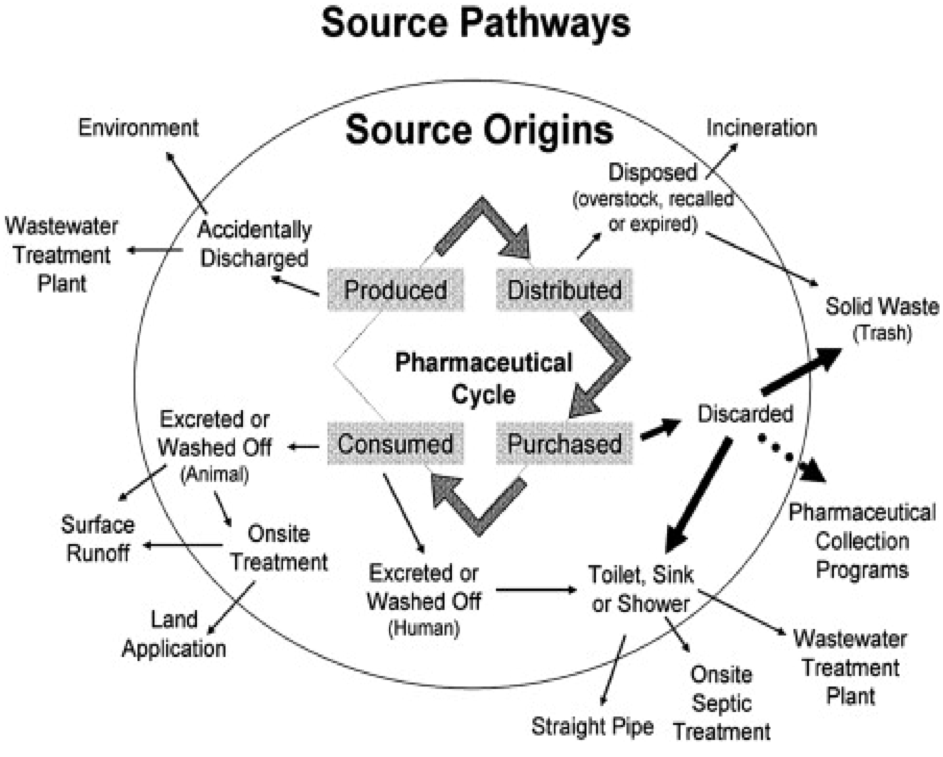


Figure2.1: Pathways by which pharmaceutical waste enter the environment (source: USGS[3])

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[3] United State Geological Survey

2.4 Environmental impacts of pharmaceuticals effluent

Several categories of pharmaceuticals raise particular concerns: those produced and consumed in especially large quantities, those highly potent at low concentrations, and those particularly persistent and bio-accumulative in the environment. Within these categories, two types of pharmaceuticals – antimicrobials and endocrine disrupting chemicals (EDCs) – can be appropriately singled out as priorities.

The migration of antimicrobials into the environment has significant impacts. They can disrupt wastewater treatment processes and adversely affect ecosystems because they are toxic to beneficial bacteria. Some antimicrobials also bioaccumulate; for example, erythromycin has been found to have both a high bioaccumulation factor of 45.31and a tendency to accumulate in soils. (Jones O. A. H et al., 2002) Antimicrobials can also be persistent for extended periods of time; the environmental persistence of erythromycin, for example, is longer than one year. (Zuccato E. et al., 2000)

The second class of troubling pharmaceuticals are hormones and endocrine disrupting drugs, which are excreted as waste by-products from the use of, among others, birth-control pills, menopause treatments, thyroid replacement, and cancer therapy. The presence of pharmaceuticals in drinking water also raises issues beyond the obvious concern about public health. Since human exposures through drinking water are more intermittent, some experts have identified ecosystem effects as a higher concern than human health. (Webb S. et al., 2003)

2.5 Pharmaceutical active compounds (PhAC's):

Pharmaceutically active compounds (PhACs) such as analgesics, anti-convulsants, antidepressants, anti-inflammatories, hormones, and antibiotics can enter municipal and natural water systems via residential or commercial discharges, including hospital effluent. Although PhACs are intended to be utilized by the human body, in some instances as much as 50 to 90 percent of an administered drug may be excreted by the body in a biologically active form (Raloff 1998). Wastewater treatment facilities vary in their ability to remove PhACs. Consequently, PhACs are released into surface waters where they may adversely impact aquatic organisms (Jobling et al., 1998).

Wastewater treatment plants usually exceed current discharge standards; the presence of unregulated pollutants in these effluents is of concern unregulated contaminants, or emerging pollutants of concern (EPOCs), are defined as substances that were previously undetected or had not been considered as a risk. The main sources of non-regulated contaminants in the environment are wastewater treatment plant effluents, which are not designed to eliminate these compounds. They are present in treated wastewaters at trace levels (µg/l to hg/l), and include personal care products, pharmaceuticals, surfactants, flame retardants, industrial chemicals, gasoline additives, and disinfection by products.

2.6 Overview of Pesticide industry:

Pesticides are defined as the substance or mixture of substances used to prevent, destroy, repel, attract, sterilise, stupefy or mitigate any insects. Generally pesticides are used in three sectors viz. agriculture, public health and consumer use. The consumption of pesticide in India is about 600 gm / hectare, where as that of developed countries is touching 3000 gm / hectare.

Pesticides are basically toxics and persistence; it can enter in food chain and causes injury to human health. It also destroys the diversity and food web and causes ecological imbalance. Pest control therefore needs regulation on the interest of human health and environment.

2.7 Process description and waste characteristics:

Pesticides manufacturing is a part of organic fine chemical manufacturing. The principal manufacturing steps include (Fig. 2.2):

(a) Preparation of process intermediates

(b) Introduction of functional groups

(c) Coupling and esterification

(d) Separation processes (e.g. washing and stripping); and

(e) Purification of the final product (e.g. dissolution, dissolution and extraction, or ultra-filtration).

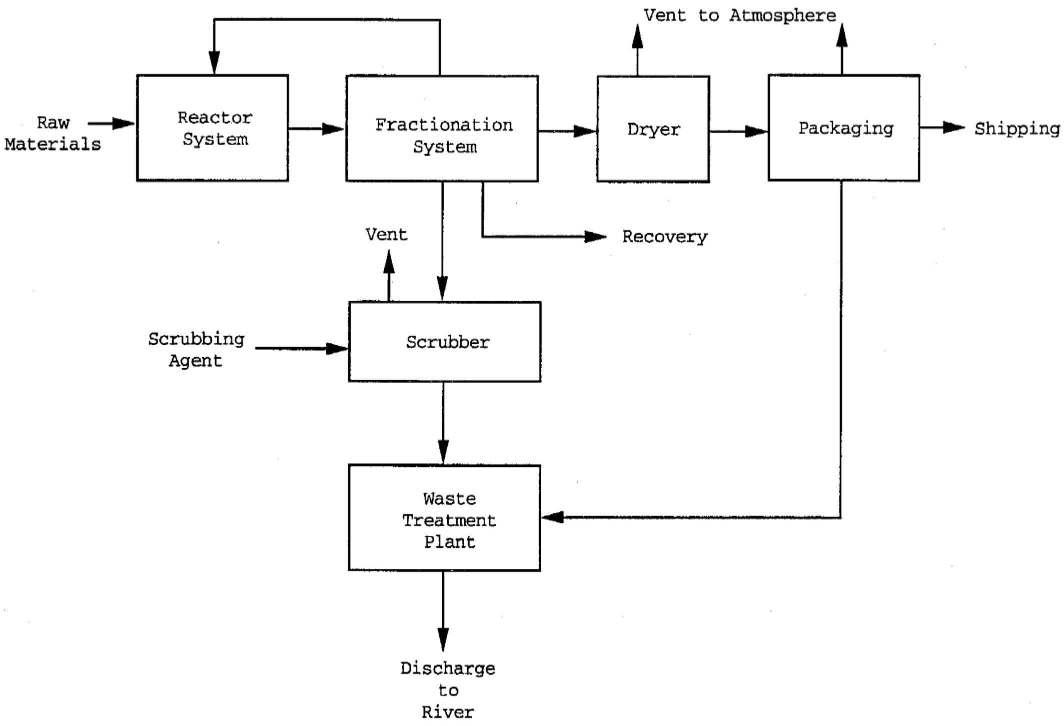

Figure 2.2: Pesticide manufacturing flow schematic (source: USEPA[4])

Based on the studies conducted on various pesticide manufacturing units, as the identified pollutants associated with products are given in Table: 2.3

Table 2.3: Product and associated priority pollutants (source: CPCB)

S. No.	**Pesticide**	**Name of the Pollutants**
01.	Acephate	HCl
02.	Aluminium phosphide	P_2O_5 fumes (as H_3PO_4 mist)
03.	Captafol	Cl_2 and HCl
04.	Captan	Cl_2 and HCl
05.	Cypermethrin	Cl_2, HCl and SO_2
06.	Dimethoate	H_2S
07.	2, 4 – D Acid	HCl and Cl_2

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[4] United State Environmental Protection Agency

08.	Dichlorvos (D.D.V.P)	CH_3Cl
09.	Ethion	H_2S and C_2H_5SH
10.	Endosulphan	HCl
11.	Fenvalerate	HCl
12.	Zinc Phosphide	P_2O_5 as H_3PO_4

Liquid effluents resulting from equipment cleaning after batch operation contain toxic organics and pesticide residues. Cooling waters are normally recirculated. Wastewater concentrations are: 13,000 milligrams per liter (mg/L) (with a range of 0.4 to 73, 000 mg/L) COD; 800 mg/L (with a range of 1 to 13,000 mg/l) oil and grease; and 2,800 mg/L) with a range of 4 to 43,000 mg/L of total suspended solids.

2.8 Health impacts of pesticides effluent:

Summary of toxic properties of priority pollutants identified from the studied process are given in **Table 2.4.**

Table 2.4: Properties and Health impact of some priority pollutants (source: CPCB[5])

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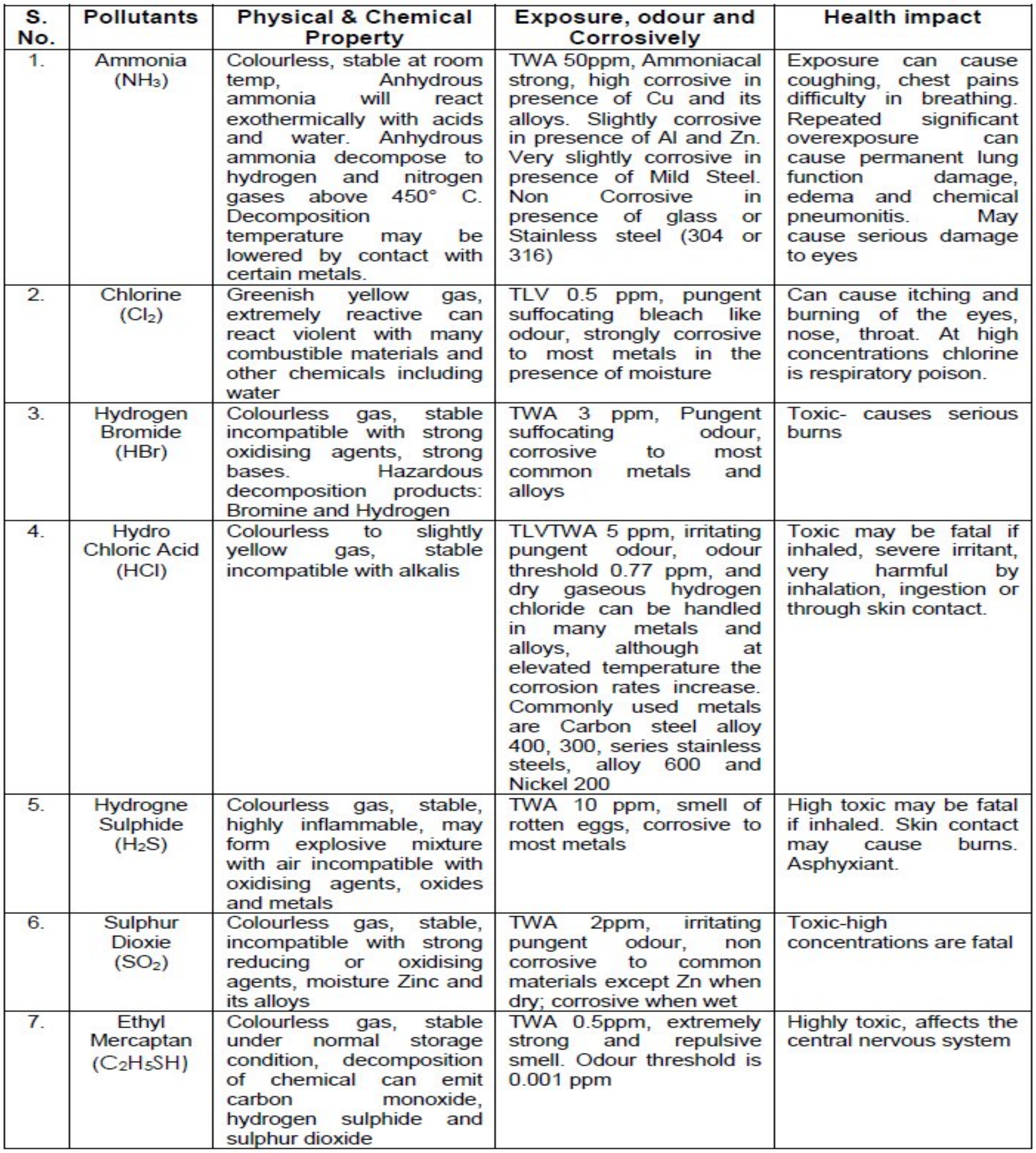
[5] Central Pollution Control Board



S. No.	Pollutants	Physical & Chemical Property	Exposure, odour and Corrosively	Health impact
1.	Ammonia (NH_3)	Colourless, stable at room temp, Anhydrous ammonia will react exothermically with acids and water. Anhydrous ammonia decompose to hydrogen and nitrogen gases above 450° C. Decomposition temperature may be lowered by contact with certain metals.	TWA 50ppm, Ammoniacal strong, high corrosive in presence of Cu and its alloys. Slightly corrosive in presence of Al and Zn. Very slightly corrosive in presence of Mild Steel. Non Corrosive in presence of glass or Stainless steel (304 or 316)	Exposure can cause coughing, chest pains difficulty in breathing. Repeated significant overexposure can cause permanent lung function damage, edema and chemical pneumonitis. May cause serious damage to eyes
2.	Chlorine (Cl_2)	Greenish yellow gas, extremely reactive can react violent with many combustible materials and other chemicals including water	TLV 0.5 ppm, pungent suffocating bleach like odour, strongly corrosive to most metals in the presence of moisture	Can cause itching and burning of the eyes, nose, throat. At high concentrations chlorine is respiratory poison.
3.	Hydrogen Bromide (HBr)	Colourless gas, stable incompatible with strong oxidising agents, strong bases. Hazardous decomposition products: Bromine and Hydrogen	TWA 3 ppm, Pungent suffocating odour, corrosive to most common metals and alloys	Toxic- causes serious burns
4.	Hydro Chloric Acid (HCl)	Colourless to slightly yellow gas, stable incompatible with alkalis	TLVTWA 5 ppm, irritating pungent odour, odour threshold 0.77 ppm, and dry gaseous hydrogen chloride can be handled in many metals and alloys, although at elevated temperature the corrosion rates increase. Commonly used metals are Carbon steel alloy 400, 300, series stainless steels, alloy 600 and Nickel 200	Toxic may be fatal if inhaled, severe irritant, very harmful by inhalation, ingestion or through skin contact.
5.	Hydrogne Sulphide (H_2S)	Colourless gas, stable, highly inflammable, may form explosive mixture with air incompatible with oxidising agents, oxides and metals	TWA 10 ppm, smell of rotten eggs, corrosive to most metals	High toxic may be fatal if inhaled. Skin contact may cause burns. Asphyxiant.
6.	Sulphur Dioxie (SO_2)	Colourless gas, stable, incompatible with strong reducing or oxidising agents, moisture Zinc and its alloys	TWA 2ppm, irritating pungent odour, non corrosive to common materials except Zn when dry; corrosive when wet	Toxic-high concentrations are fatal
7.	Ethyl Mercaptan (C_2H_5SH)	Colourless gas, stable under normal storage condition, decomposition of chemical can emit carbon monoxide, hydrogen sulphide and sulphur dioxide	TWA 0.5ppm, extremely strong and repulsive smell. Odour threshold is 0.001 ppm	Highly toxic, affects the central nervous system

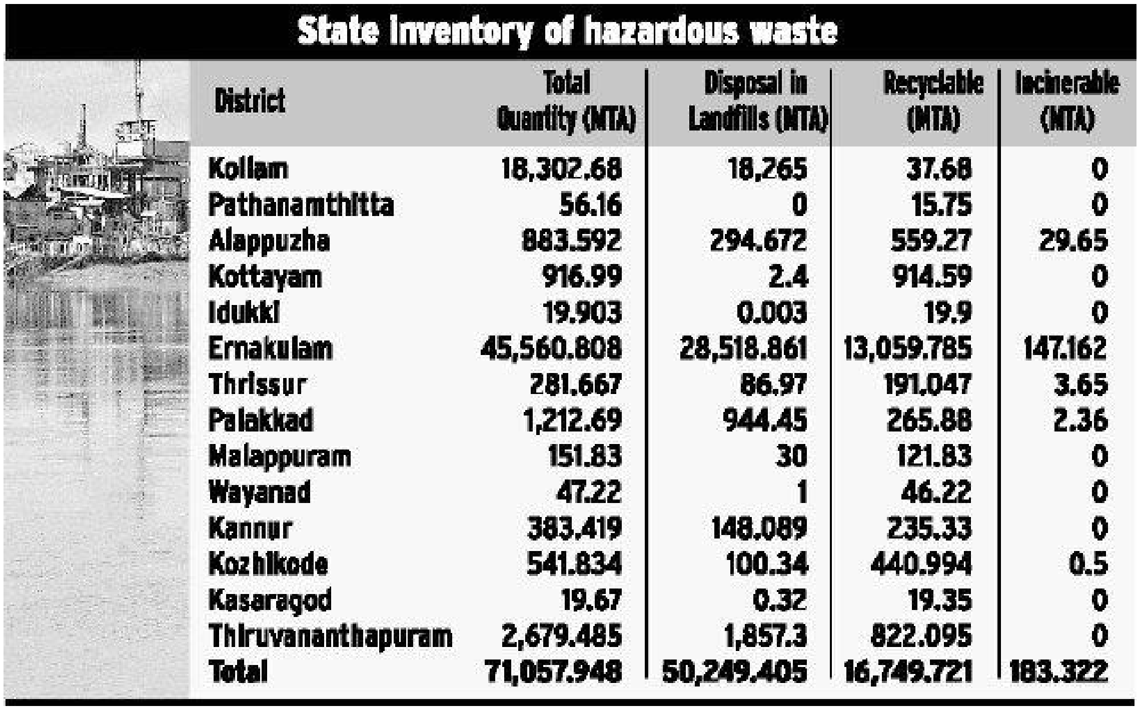
2.9 Case Study (Source: THE HINDU KOCHI, February 10, 2012):

Pesticides and metallurgical industries top polluters:

Ernakulam district has emerged as the new hazardous waste capital of Kerala. The district is the top contributor to the amount of hazardous waste generated in the State, producing about 45,560 metric tonnes of hazardous waste annually.

Kerala generated about 71,050 metric tonnes of hazardous waste in 2009-10, according to the State inventory of hazardous waste generating industries prepared by the Kerala State Pollution Control Board.

Ernakulam is followed by Kollam (18, 302 metric tonnes) and Thiruvananthapuram (2, 679 metric tonnes).



State Inventory of hazardous waste

District	Total Quantity (MTA)	Disposal in Landfills (MTA)	Recyclable (MTA)	Incinerable (MTA)
Kollam	18,302.68	18,265	37.68	0
Pathanamthitta	56.16	0	15.75	0
Alappuzha	883.592	294.672	559.27	29.65
Kottayam	916.99	2.4	914.59	0
Idukki	19.903	0.003	19.9	0
Ernakulam	45,560.808	28,518.861	13,059.785	147.162
Thrissur	281.667	86.97	191.047	3.65
Palakkad	1,212.69	944.45	265.88	2.36
Malappuram	151.83	30	121.83	0
Wayanad	47.22	1	46.22	0
Kannur	383.419	148.089	235.33	0
Kozhikode	541.834	100.34	440.994	0.5
Kasaragod	19.67	0.32	19.35	0
Thiruvananthapuram	2,679.485	1,857.3	822.095	0
Total	71,057.948	50,249.405	16,749.721	183.322

Figure 2.3: pesticide waste in Kerala

The data collected by the board will soon form part of the national inventory on hazardous waste generating industries and hazardous waste management in India to be published by the Central Pollution Control Board. The State has about 480 authorised hazardous waste generating industries.

The board has broken down the hazardous waste generation into land disposable hazardous waste (HW), incinerable hazardous waste and recyclable hazardous waste. Ernakulam generates about 28,518 metric tonnes of disposable hazardous waste every year, while the recyclable waste is about 13,050 metric tonnes.

In Kollam district, the disposable hazardous waste is about 18,265 metric tonnes while the recyclable hazardous waste is about 37 metric tonnes. Thiruvananthapuram has 1,857 metric tonnes of disposable hazardous waste and 833 metric tonnes of recyclable hazardous waste. Palakkad generates 944 metric tonnes of hazardous waste while the quantity of recyclable waste is about 265 metric tonnes every year.

The total quantity of disposable hazardous waste generated in the State is about 50,240 metric tonnes annually. About 16,749 metric tonnes of recyclable hazardous waste is generated every year while the quantity of incinerable hazardous waste is about 183 metric tonnes.

The board found that hazardous waste pollution occurred both at the level of industrial production, as well as end use of products and run-off. Major sources of the hazardous waste generation in the State include metallurgical industry, pesticide manufacturing units and oil residues.

2.10 Conventional Treatment:

The extent to which pharmaceuticals enter the environment is largely determined by the nature of the wastewater treatment plant (WWTP) where they are discharged and the type of contaminant. A study of the effects of sewage treatment on 55 pharmaceuticals, for example, found an average removal rate of approximately 60 percent at a conventional sewage treatment plant (clarification, aeration, and coagulation/flocculation/sedimentation). WWTPs successfully remove some drugs such as ibuprofen and salicylic acid. 80 Other drugs, however, such as the anticonvulsant carbamazepine, the lipid regulator gemfibrozil, the analgesic diclofenac, and the drug metabolite clofibric acid have not been found to be effectively degraded in most conventional plants.

There are many limitations with the conventional system which have a propensity to use more chemical such as coagulant, polymer and chlorine during the extreme weather, which is actually not good for the consumer. And other drawback is its non ability to treat or degrade toxic and non biodegradable pollutants. So new technologies have made growing numbers of water treatment alternatives available and one of them is advance treatment method. It's a technology that reduces our dependent on chemical for treatment process and also helps us to treat various toxics present in wastewater. May be we can go for a chemical free treatment process in the future.

According to the above discussion, it is clear that both pharmaceutical and pesticide industries generate large amount of toxic waste, which contains many different hazardous and complex compounds. 2-C 4-NP is one among those complex and toxic compound, which is used as an intermediate in both the pharmaceutical and pesticide industry. The waste characteristic of both the above studied industries shows that the conventional methods are not capable to degrade all the complex compounds like 2-C 4-NP, which are non-biodegradable, hence require some advance treatment.

OBJECTIVES OF PRESENT STUDY

Main objective of our study is to treat non-biodegradable compound present in pharmaceutical and pesticidal wastewater which are not degraded by conventional treatment processes. Based upon literature search 2-chloro-4-nitrophenol was selected for the study.

The study was undertaken with the following objectives:

- ✓ To study the degradation of model compound using slurry mode solar-photocatalytic process.
- ✓ To study the effect of various parameters such as concentration of catalyst, pH, H_2O_2, effect of UV intensity on degradation rate of these compounds and their kinetic studies
- ✓ To study the degradation of model compound using different supporting materials (glass, cement and sodium alginate balls) for fixed bed solar-photocatalysis process.

Chapter 3

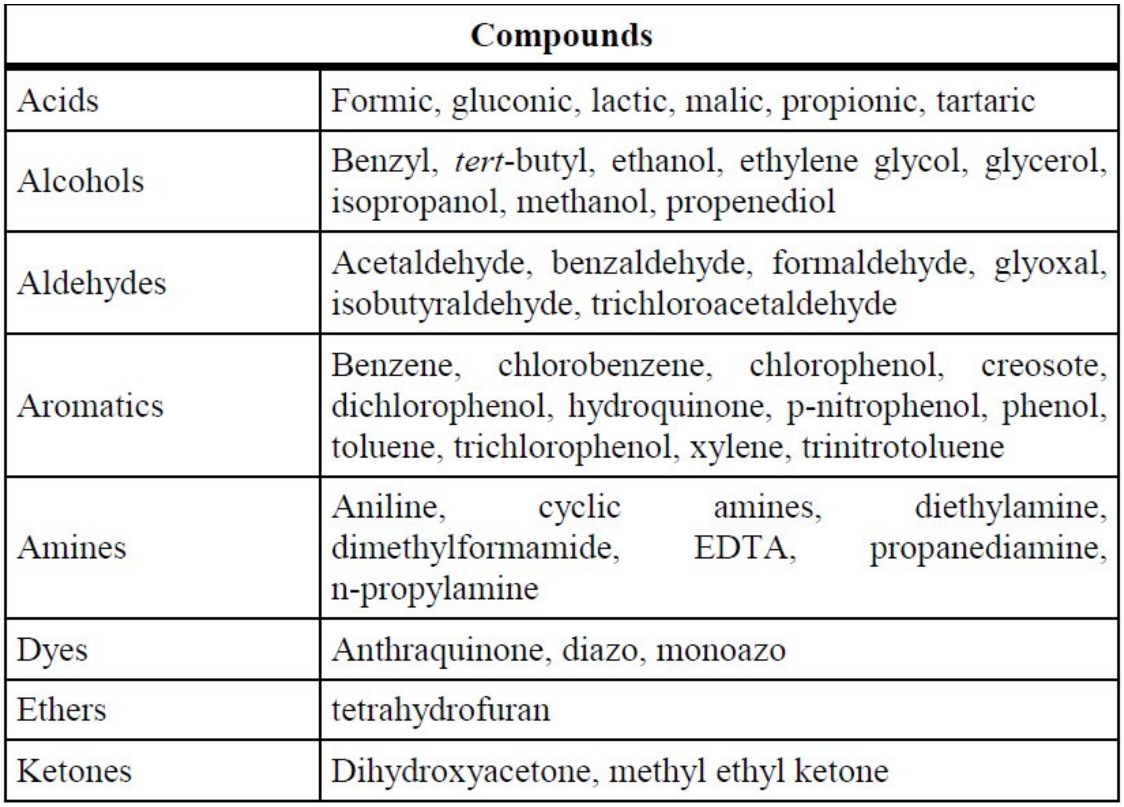
Treatment Technology

3.1 General Overview:

AOPs were defined by Glaze and et al. (1987) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive species that attack most of the organic molecules. The kinetics of reaction is generally first order with respect to the concentration of hydroxyl radicals and to the concentration of the species to be oxidized.

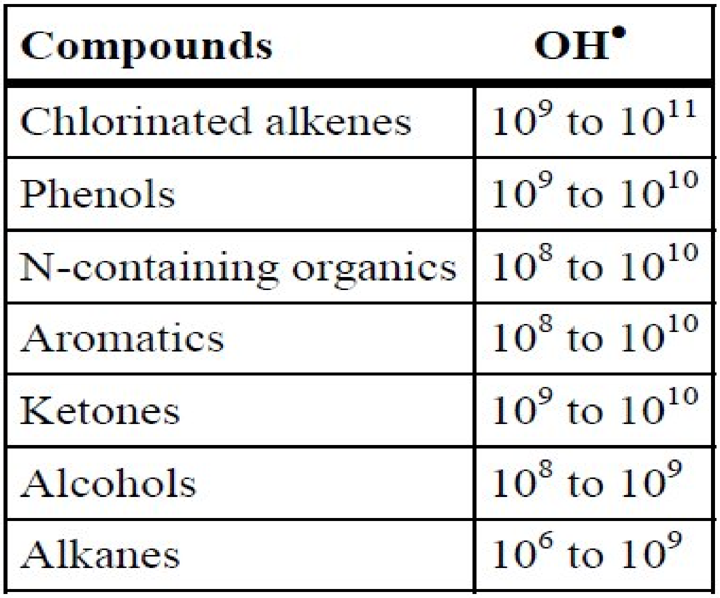
Rate constants are usually in the range of $10^8 – 10^{11}$ L.mol^{-1}.s^{-1}, whereas the concentration of hydroxyl radicals lays between 10^{-10} and 10^{-12} mol.L^{-1}, thus a pseudo-first order constant between 1 and 10^{-4} s^{-1} is obtained (Glaze and Kang, 1989). Hydroxyl radicals are also characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment. Several and different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals, as it is shown in Table 3.1. Depending upon the nature of the organic species, two types of initial attacks are possible: the hydroxyl radical can abstract a hydrogen atom to form water, as with alkanes or alcohols, or it can add to the contaminant, as it is the case for olefins or aromatic compounds.
The attack by hydroxyl radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization. As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constants for the contaminant with the hydroxyl radical. From Table 3.2 it can be seen that chlorinated alkenes treat most efficiently because the double bond is very susceptible to hydroxyl attack.

Table 3.1. Oxidizable compouns by hydroxyl radicals



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

Table 3.2. Reaction rate constant (k, L mol^{-1} s^{-1})



Compounds	$OH^\bullet$
Chlorinated alkenes	10^9 to 10^{11}
Phenols	10^9 to 10^{10}
N-containing organics	10^8 to 10^{10}
Aromatics	10^8 to 10^{10}
Ketones	10^9 to 10^{10}
Alcohols	10^8 to 10^9
Alkanes	10^6 to 10^9

The versatility of AOPs is also enhanced by the fact that they offer different ways of $HO^\bullet$ radicals production, thus allowing a better compliance with the specific treatment requirements. As hydroxyl radicals are so reactive and unstable, they must be continuously produced by means of photochemical or chemical reactions. The main processes of producing these radicals are described below.

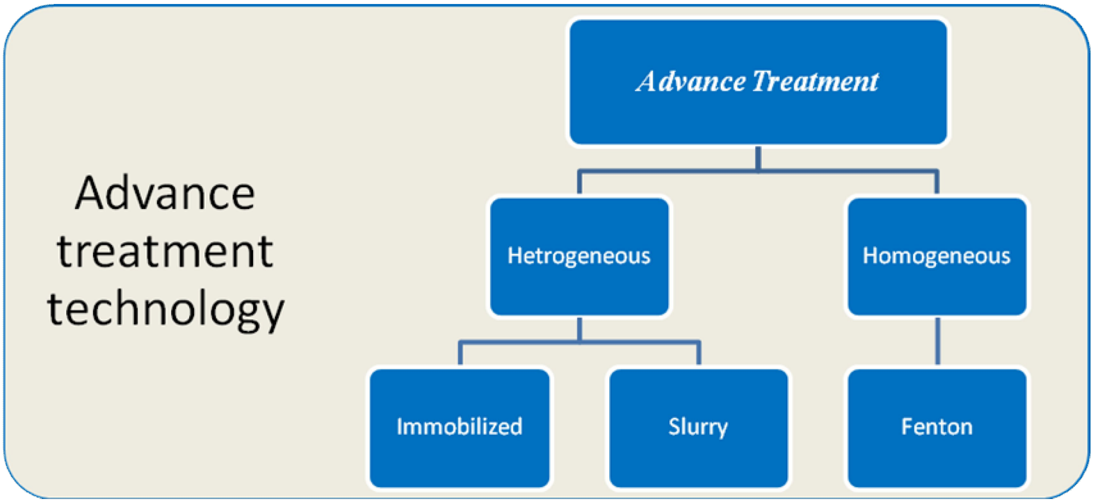


Figure 3.1: Classification of Advance treatment technology

3.2Homogenous photocatalysis:

In homogenous photocatalysis, a powerful UV lamp is used to illuminate the contaminated water in the presence of $Fe^{3+,}$ O_3 or H_2O_2 which act as a catalyst and the reaction takes place in the bulk solution.

3.3Hetrogenous photocatalysis:

Heterogeneous photocatalysis can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pair by suitable light on the surface of the solid semiconductor materials.

The distribution and utilization of light energy due to the presence of solid catalyst material in liquid or gaseous mixtures makes this process more complex compared with homogeneous process.

Basic Principal

The mechanism of photocatalysis can be categorized into five steps, which are shown in Fig.3.2:

1. Mass transfer of the organic contaminant(s) in the liquid phase to the TiO_2 surface.
2. Adsorption of the organic contaminant(s) onto the photon activated TiO_2 surface (i.e. surface activation by photon energy occurs simultaneously in this step).
3. Photocatalysis reaction for the adsorbed phase on the TiO_2 surface.
4. Desorption of the intermediate(s) from the TiO_2 surface.
5. Mass transfer of the intermediate(s) from the interface region to the bulk fluid. (Herrmann J.et al., 1999).

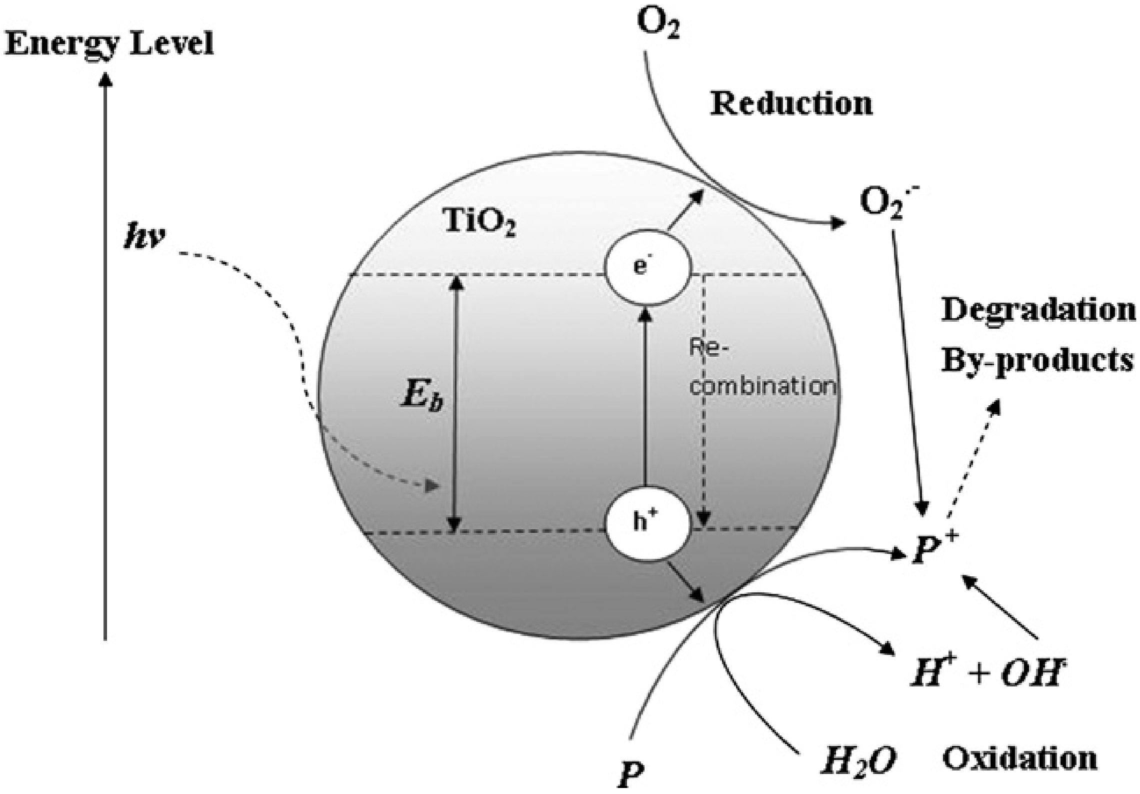


Figure3.2: Photo-induced formation mechanism of electron hole pair in a semiconductor TiO_2 particle with the presence of water pollutant

Most of the studies related to photodegradation have been carried out using the suspension of powder TiO_2 in aqueous solutions. However, the use of aqueous suspension is limited for practical application by filtration problems due to the small size of TiO_2 particles.

Fixed bed photocatalysis

Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of removing the catalyst. Unfortunately, when the catalyst is immobilized there is a decrease in the available surface area for the reaction since the catalyst must adhere to the solid support and the reactor design is limited by the optical absorption constraints. Many techniques were proposed for the immobilization of TiO_2 on solid supports like glass, quartz, silica, activated carbon, fiber glass cloth, zeolites and stainless steel. (Noorjahan M. et al., 2003).

Since 1993, the idea of an immobilised photocatalyst on an inert support has begun to be widely accepted because it could help to eliminate the costly phase separation processes (Fabiyi M.E et al., 2000). To this end, many excellent studies have been published on the anchoring of the photocatalyst particles onto supports that are readily removable.

As a response, several workers have coated photocatalysts onto a variety of surfaces, such as glass, silica gel, metal, ceramics, polymer, thin films, fibres, zeolite, alumina clays, activated carbon, cellulose, reactor walls and others (Jean J.H. et al., 1986 and Parra S. et al., 2004).

3.5 Photocatalyst support:

Various materials have been explored as a TiO_2 support for the photodegradation of contaminants in polluted water. Immobilisation can be carried out on a transparent substrate (glass, fused silica and others) or on an opaque substrate (activated charcoal, metals and others). From the practical point of view, the ideal support for photocatalysis must satisfy several criteria as follows:

(1) Strong adherence between catalyst and support;
(2) Non-degradation of the catalyst reactivity by the attachment process;
(3) Offer a high specific surface area; and
(4) Have a strong adsorption affinity towards the pollutants (Fabiyi M.E. et al., 2000).

3.6 Solar Photocatalysis:

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 (Pera-Titus, M. et al., 2004). The main disadvantage of AOPs is their high cost.

The use of AOPs for WW treatment has been studied extensively, but generation of UV radiation by lamps or ozone production is expensive (Muñoz I. et al., 2005). Therefore, research is focusing more and more on those AOPs, which can be driven by solar irradiation, i.e., light with a wavelength longer than 300 nm, Contrary to solar-thermal processes, which collect large amounts of photons at any wavelength to reach a specific temperature range, solar photocatalytic processes use only the high-energy short-wavelength photons to promote photochemical reactions i.e., 600 nm.

The traditional classification considers only the thermal efficiency of the solar collectors. However, in photocatalytic applications, the thermal factor is irrelevant whereas the amount of useful radiation collected (in the case of the TiO_2 catalyst, with a wavelength shorter than 385 nm) is very important.

Non- concentrating solar collectors are static and non-solar-tracking. Usually, they are flat plates, often aimed at the sun at a specific tilt, depending on the geographic location. Their main advantage is their simplicity and low cost. An example is domestic hot water technology. Fig. 3.3 shows a diagram of non-concentrating solar collector for domestic heat water applications. (Blanco and Malato, 2001)

Figure 3.3: Non - concentrating solar collector

Medium concentrating solar collectors concentrate sunlight between 5 and 50 times, so continue tracking of sun is required. Parabolic Trough Collectors (PTC) and Holographic collectors (Fresnel lenses) are in this group. The first have a parabolic reflecting surface, which concentrates the radiation on a tubular receiver, located in the focus of the parabola. Fig.3.4 shows a medium concentrating solar reactor installed in Spain (Blanco and Malato, 2001).

Figure 3.4: Medium concentrating solar reactor

High concentrating collectors have a focal point instead of a linear focus and are based on a parabola with solar tracking. Typical concentrating ratios are in the range of 100 and 10000 and precision optical elements are required. They include parabolic dishes and solar furnaces. Fig.3.5 shows high concentrating (dish type) solar reactor.

Figure 3.5: high concentration solar reactor. Fix focus solar reactor (PSA, Spain)

Up to now, the solar collectors used for photocatalysis have been in the two first categories. The requirements for the photocatalytic reactor are similar to other advanced water or air oxidation processes, with the additional necessity of an illuminated photocatalyst. The photocatalytic reactor must contain the catalyst and be transparent to UV radiation providing good mass transfer of the contaminant from the fluid stream to an illuminated photocatalyst surface with minimal pressure drop across the system.

CHAPTER 4

LITERATURE REVIEW

Any treatment process must guarantee the elimination of pollutants, in the effluent to meet discharge standards, which are directly related to the type of pollutant in the wastewater. The elimination of pollutants in wastewater needs different basic treatment techniques (Weber and Smith, 1986; Chaung et al., 1992) like chemical oxidation, air desorption, liquid-liquid extraction, adsorption, inverse osmosis, ultra-filtration and biological-treatment. The selection of the techniques depends upon the concentration of the effluent (incineration and chemical oxidation for higher concentration of pollutant/ adsorption and membrane filtration for lower concentration). Cost of the process and volume of the effluent also determine the type of treatment technique to be used.

4.1 International status

Heterogeneous photocatalysis with titanium dioxide as a semiconductor has proven to be an efficient process for elimination of different types of dyes, organic chemical, industrial effluent, landfill leachate and pathogen from drinking water. This method has great advantages: first this process can be carried out under ambient conditions and may lead to total mineralization of organic carbon to CO_2 , second photocatalyst, usually TiO_2, is non-toxic, cheap and can be supported on suitable materials like glass quartz , silica, activated carbon, fibre glass cloth, zeolites, stainless steel, polythene film and pumice stone. Several different reactor models have been proposed and evaluated for the purpose of removing organic contaminants from water. Different models can be classified into two broad categories—slurry reactors utilizing suspended TiO_2 powders and immobilized TiO_2 catalyst reactors. Most of the studies related to photodegradation have been carried out using the suspension of powder TiO_2 in aqueous solutions. However, the use of aqueous suspension is limited for practical application by filtration problems due to the small size of TiO_2 particles. Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of removing the catalyst.

Hussain AI-Ekabi and Nick Serpone (1988) studied the photocatalytic degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,5-trichlorophenol over $Ti0_2$ (anatase) has been investigated by using three photochemical reactors. $Ti0_2$ was used as a thin film, coating the internal surface of a glass coil (reactor I and II) or the external surface of glass beads (reactor III). The degradation of the four phenolic compounds, in a continuous recirculation mode in all three reactors, approximates first-order kinetics to near-complete degradation. In the multipass mode experiments, both reactors I and I1 exhibit higher degradation rates for phenol at the higher flow rates. By contrast, the greater degradation is associated with the lower flow rates in the single-pass mode experiments.

Sylwia Mozia et al. (2006) was investigated the photocatalytic oxidation of Azo dye Acid Red 18 in water in the quartz labyrinth flow reactor with immobilized catalyst bed. The decomposition rate of Acid Red 18 depended on the initial dye concentration. The rate constants calculated for dye concentrations of 10 and 30 mg/dm^3 amounted to 0.228 and 0.176 /hour, respectively. Not only decolorization but also mineralization was effective in the proposed system. After a total fading of the dye solution, ca. 98% of TOC disappeared when the 10 mg/dm^3 solution was applied and ca. 99% when 30 mg/dm^3 was used.

Álvarez P.M. et al., (2011) was done a comparative study with a pilot scale plant to compare the effectiveness and energy consumption of some advanced treatment methods applied for municipal wastewater reclamation. The studied processes were: adsorption onto activated carbon, ozonation, O_3/H_2O_2, catalytic ozonation (using activated carbon as catalyst), UV-C photolysis and TiO_2 photocatalysis. The sewage effluent used in this study was taken from the exit of a municipal wastewater treatment plant and it was then spiked with up to five pharmaceutical compounds before treatment.

Pharmaceutical compounds were satisfactorily removed (< 90% removal) with all the treatment methods used but adsorption onto activated carbon (81.4%) and direct photolysis (22%). COD removals were in the range 20.4- 83.3% while satisfactory disinfection (total coliforms in the effluent below 100 CFU/100 ml) was only obtained by ozone and photocatalysis technologies. A comparison of the energy requirements in terms of electrical energy per order or magnitude per m^3 (EE/O) was carried out. It was found that ozonation processes as well as solar TiO_2 photocatalysis were the less energy-consuming technologies to achieve the target quality effluent.

FEITZ A. J. et al. (2000) evaluate two solar pilot scale fixed bed photocatalytic reactors 1.coated mesh reactor and 2.Packed bed reactor for the removal of phenols. By coated mesh reactor the total removal of phenol, for an exposure of 200min is 36%.

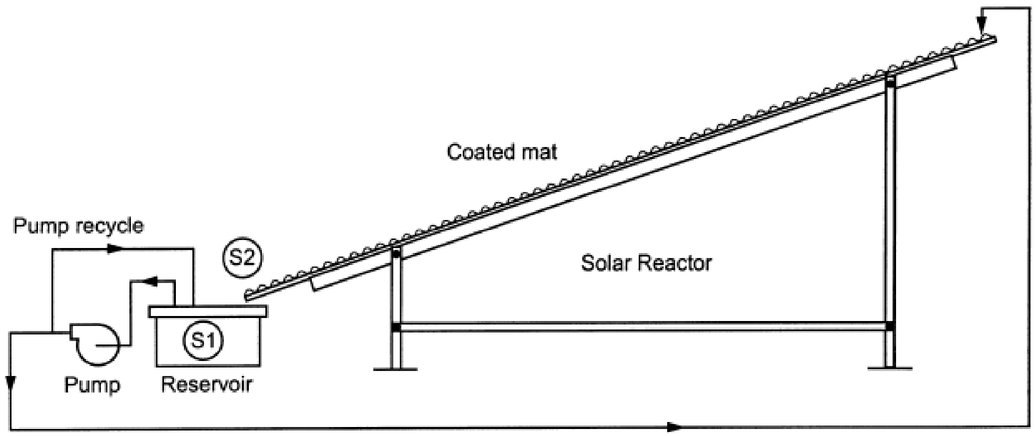


Figure 4.1: coated mesh reactor

Table 4.1 Design Discussion of Coated mesh reactor

Supporting Material	Glass-fibre mesh

Area of Reactor	6.5x0.5 mt^2
Flow Rate	5lt/min

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

Table 4.2 Design Discussion of Packed bed reactor

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

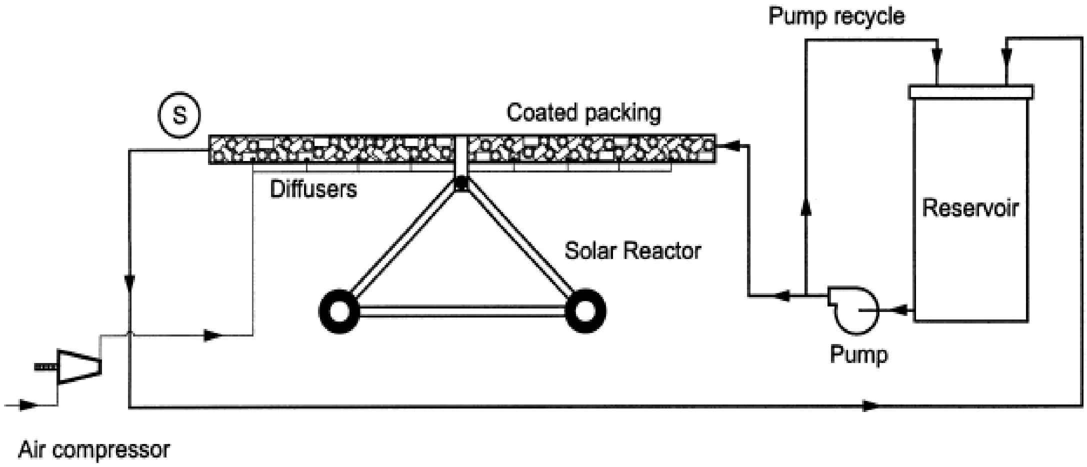


Figure 4.2: Packed bed reactor

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

Table 4.3 Design Discussion of fixed bed solar reactor

Supporting Material	Glass plate
Flow Rate	2-6 l/min
Area of Reactor	0.48 m^2

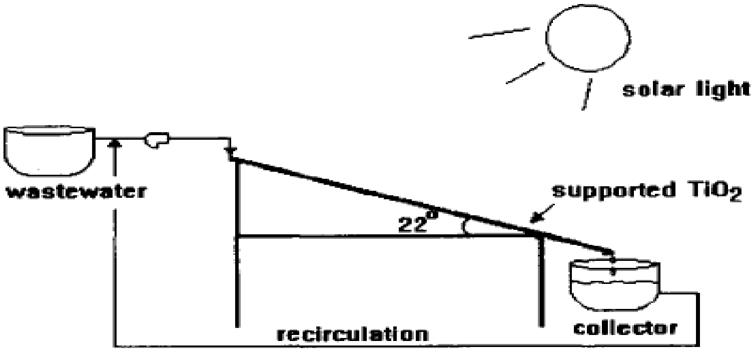


Figure 4.3: Schematic view of TiO_2-fixed-bed solar reactor.

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

Kuo-Hua Wang et al. (1998) has done an investigation by using a specially built jacketed cylindrical type reactor with suspended titanium dioxide under UV-light of 365 nm for feasibility studies of decomposition of mono-substituted phenols. The factors to be studied were the effects of pH, anion additives and the influence of co-existing reactants competing for reaction. Finally, the degree of mineralization of reactants was conducted in order to survey the effectiveness of treatment.

From experimental results, under the condition of 7.5 g/l TiO_2, pH 3, and light intensity of 2.25 mW/cm^2, 0.1 mM of substituted phenol could be completely decomposed in 2 h. The reaction was found to be apparent first-order following Langmuir-Hinshelwood model. In the presence of chloride ions, a significant inhibition of reaction was found at pH 3, but not at higher pH levels.

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

Table 4.4 Design Discussion of Thin film fixed bed reactor

Supporting Material	Concrete
Area of Reactor	$25m^2$
Flow Rate	2.5 l/min

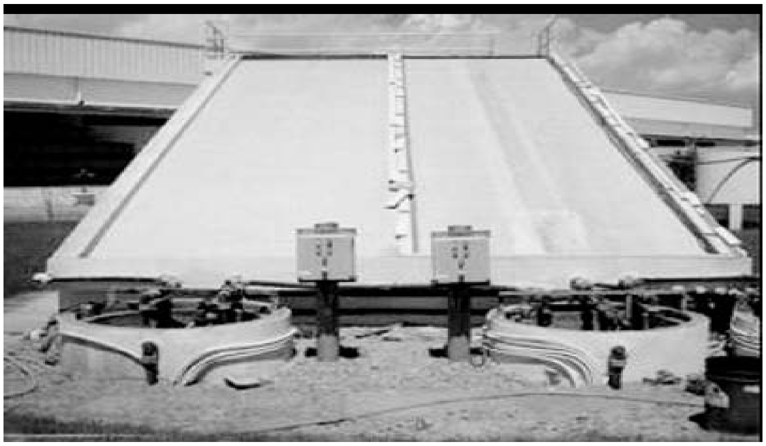


Figure 4.4: Photo and simplified flow chart of TFFBR

Tennakone K. et al. (1995) studied photocatalytic degradation of organic contaminants in water with TiO_2 supported on polythene films. The insignificant quantity of carbon dioxide detected from degradation of phenol by UV light, which could be impurities present in polythene. Results obtained are reproducible and improvement of the technique of deposition may be give better results. It is seen that more than 50% phenol has got degraded in 2.5 hours.

Chin Mei Ling et al. (2011) was successfully studied synthesization and immobilization of TiO_2 thin film photocatalyst on glass reactor tube using sol-gel method. The synthesized TiO_2 coating was transparent, which enabled the penetration of ultra-violet (UV) light to the catalyst surface. Two photocatalytic reactors with different operating modes were tested: (a) tubular photocatalytic reactor with re-circulation mode and (b) batch photocatalytic reactor. A new proposed TiO_2 synthesized film formulation of 1 titanium isopropoxide: 8 isopropanol: 3 acetyl acetone: 1.1 H_2O: 0.05 acetic acid (in molar ratio) gave excellent photocatalytic activity for degradation of phenol and methylene blue dye present in the water. In the tubular photocatalytic reactor, 5 re-circulation passes with residence time of 2.2 min (single pass) degraded 50% of 40-lM methylene blue dye.

Alex H.C. Chan et al. (2003) constructed a solar photocatalytic cascade reactor to study the photocatalytic oxidation of benzoic acid in water under different experimental and weather conditions. Nine stainless steel plates coated with TiO_2 catalyst were arranged in a cascade configuration in the reactor.

Figure 4.5: photograph of cascade reactor

Table 4.5 Design Discussion of Cascade reactor

Supporting Material	Stainless Steel
Area of Reactor	17.5x28 cm^2
Flow Rate	2-5 l/min

A turbulent flow pattern and, hence, improved mixing in the liquid film were achieved due to unique cascade design of the reactor. The percentage removal of TOC of 100 ppm benzoic acid solutions increased from 30% to 83% by adding 10ml of hydrogen peroxide solution

(30wt%). Hydrogen peroxide was also shown to enhance the efficiency of the degradation process at elevated temperatures.

Thierry Giornelli et al. 2004 studied the dip-coating technique using metallic alcoholates for the grafting of TiO_2 on aluminium foil or aluminium plates, which is controlled by X-ray photoelectron spectroscopy (XPS). A monolayer of TiO_2 is first grafted, and then a porous film of TiO_2-anatase is deposited by sol–gel. Finally, VOx species are grafted on titania and their loading again determined by XPS. Techniques such as Laser Raman Spectroscopy, Scanning Electron Microscopy are used to characterize the samples after each step, and the porous texture is determined. The layers are mechanically and thermally stable. The dip coating is shown to be a valuable technique to deposit desired amounts of vanadium oxide on titania, and thus to control the species grafted on the support.

Fabiyi M.E. et al. (2000) has done photocatalysed mineralisation of methylene blue using TiO2 coated onto naturally buoyant polystyrene beads. Titanium dioxide is coated onto polystyrene using a thermal treatment procedure. The coated beads show high mechanical stability as well as impressive photocatalytic activity. The catalyst activity remains appreciably high for up to 10 successive runs. These works show that rates in the case of fixed catalytic systems increase with increased turbulence.

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

Balasubramanian Ganesh et al. (2003) was studied the photocatalytic activities of the sol–gel derived TiO_2 films utilizing a quartz batch reactor. The quartz batch reactor was characterized for parameters like mixing, recycle, aeration and UV radiation flux, and the TiO_2 coated substrates were used as the photocatalyst. The activities of the catalyst films were evaluated by measuring the degradation rate of 4-chlorobenzoic acid used as a model organic pollutant. Immobilized TiO_2 powder films on stainless steel containing a mixture of anatase and rutile phases were found to be more effective than films that were substantially composed of anatase phase particles.

The activity of glass beads coated with TiO_2 powder was compared to the activity of commercially available TiO_2 catalyst beads. While the activity of the commercially available TiO_2 catalyst beads was higher there was significant attrition of the TiO_2 catalyst film.

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

4.2 National status

Kamble S. P. et al., (2006) studied photocatalytic degradation (PCD) of phenoxyacetic acid (PAA) in batch as well as in continuous photoreactor using concentrated solar radiation. Phenoxyacetic acid (PAA) is a parent molecule of the well-known herbicides like 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), which are highly toxic compounds. The effect of various parameters such as adsorption, solution pH, initial concentration of pollutant, catalyst loading and types of anions in the solution were studied in batch reactor for its optimization. A comparison of PCD of PAA with 2,4-D shows that phenoxyacetic acid degrades more rapidly than 2,4-D under the otherwise identical conditions. It has been shown that PAA can be degraded using concentrated solar radiation/air/TiO_2 system in a continuous bubble column reactor. Adsorption plays an important role in the photocatalysis process.

Noorjahan M. et al., (2003) studied photocatalytic degradation of H-acid over a novel TiO_2 thin film fixed bed reactor and in aqueous suspensions.

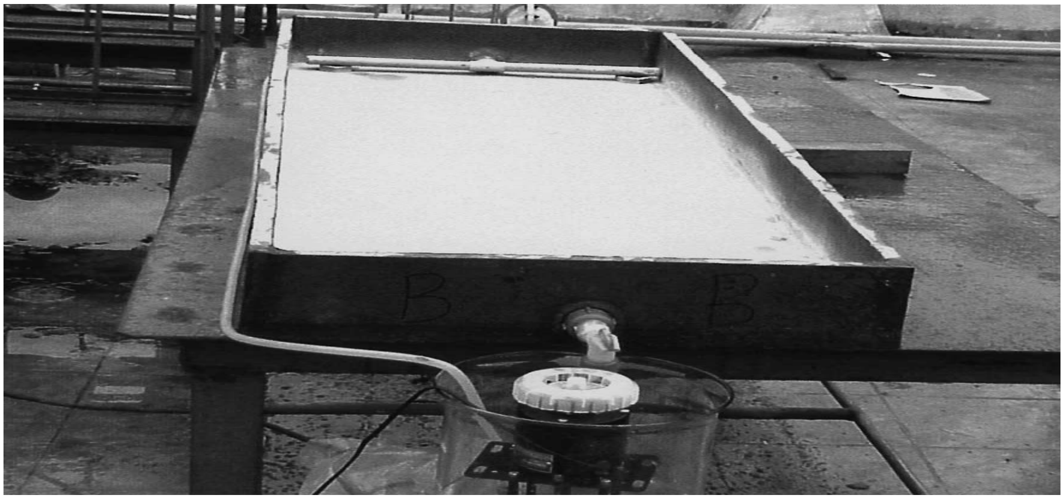


Figure 4.6: Photograph of TiO_2 TFFBR. Size: 144 cm × 52 cm × 10 cm; solution flow rate: 750 ml min−1; batch size: 5 l.

Table 4.6 Design Discussion of TFFBR

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

The study includes dark adsorption experiments in different pH conditions, influence of the amount of photocatalyst, effect of H-acid concentration, effect of pH on chemical oxygen demand (COD), biological oxygen demand (BOD) and the sulphate ion formation during the photocatalytic degradation. Photocatalytic treatment significantly reduces COD by 62% and increases BOD at the end of third day.

Subrahmanyam M. et al., (2008) studied the bactericidal and organic degradation effects of TiO_2 on pumice stone. It is fixed to a slanting unit and also loaded in a multi tube (four tubes) glass reactor and they are used for inactivation of bacteria in drinking water and degradation of model organics in wastewater. The number of colony forming units in river water was reduced by 60% after 20 min and also no cells were found at the sample collected at 40min. The pH of the solution changed from 6.60 to 5.88 after photocatalytic treatment. The change in pH of the solution with time on irradiation was affected by the bacteria inactivation.

Chapter 5

Materials and Method

5.1 Materials:

5.1.1 Pharmaceutical compound

2-Chloro-4-nitrophenol (2C4NP) is known to cause severe pollution problems in aquatic environments. 2C4NP is widely used in pharmaceuticals industries, agriculture and related industries as an ingredient in pesticides and insecticides. However, it is highly toxic because it is refractory and hard to remove by conventional biological treatment processes.

5.1.2 Structure of compound

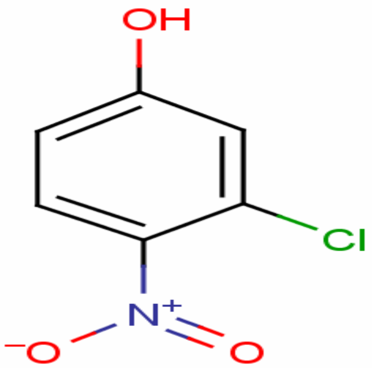


Figure 5.1: Structure of 2-chloro 4-nitro phenol

Full scan of compound was taken with the help of UV- Vis spectrophotometer and maximum absorbance was observed at 229.5 nm.

5.2 Reagents and Chemicals used

The photo catalyst was TiO_2 P-25 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, procured from Degussa Company, India branch, Bombay). Hydrogen Peroxide (Ranbaxy laboratories) was used as an oxidant. COD of raw compound was determined by using potassium dichromate solution (Containing Mercuric sulphate and Concentration Sulphuric acid), COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.1 N) and Ferroin indicator. For complete mineralization study nitrate (NO^{2-}) estimation test was also conducted, and NEDA was used as an indicator. In all experiments double distilled water was used. Different normality of HCl and NaOH were used for adjustment of pH of stock solution. (Standard Method).

5.3 Instruments used

5.3.1 pH meter

The pH of the solution was adjusted with the help of HCl and NaOH and measured with the help of pH meter. Instrument was calibrated with freshly prepared buffur solutions (of pH 4 and 9) from time to time throughout study. **(Figure-5.2)**

Figure 5.2: pH meter

5.3.2 COD Digester

COD Digester was used for the digestion of samples in the process of COD determination. **(Figure-5.3)**

Figure 5.3: COD digester

5.3.3 Spectrophotometer

The spectrum was taken with UV- vis. Spectrometer (Hitachi V- 500 UV/VIS (Japan) double- beam spectrometer. **(Figure-5.4)**

Figure 5.4: Spectrophotometer

5.3.4 Radiometer

Solar UV Intensity was measured hourly during experimental days with Eppley (model no. 33013) radiometer. Fig 5.5 is a picture of the same radiometer.

Figure 5.5: Eppley Radiometer

5.3.5 Branson bath sonicator

Sonicator was used for homogenization of catalyst suspension in the process of fabrication of fixed catalysts matrix reactor, which was coated this with catalyst solution.

5.3.6 Muffle Furnace

Rate controlled muffle furnace (temperature range 200 to 800 ^{0}c) was used for the fixation of catalyst coating on different supports. It was operated at a temperature of 300 ^{0}c for this purpose.

5.3.7 Shallow pond slurry type reactor

Glass bowls were used for the photocatalytic reaction having a capacity of 1000 ml. The catalyst was used in the form of aqueous slurry with the sample. Fig. 5.6 shows picture of the reactor.

Figure 5.6: shallow pond slurry type reactor

5.3.8 Glass plate photoreactor

Preparation for catalyst coating

This reactor was fabricated with a squarish transparent glass of the dimensions 50 cm in length, and 25 cm in width. It was prepared for having immobilized catalyst layer by rubbing with sandpaper and then degreased by dipping in 5% HNO_3 solution overnight. The glass plate was washed with water to remove to excess of HNO_3 and then dried at 120 ^{0}c.

Catalyst coating

A 5% aqueous solution of catalyst was prepared and kept for homogenization in sonicator for about 45 minutes. Glass plate was then dipped for overnight in this solution and dried at room temperature. It was then calcinated in hot oven at 100 ^{0}c for an hour.

Reactor design

Coated glass plate was kept vertically inclined at an adjustable angle between 20 ^{0} – 45 ^{0} from the ground. To completely trace the sun light the whole set up of glass plate and angle-adjustment plate was placed on a moving cooler trolley. Effluent sample was recirculated at the flow rate of 0.5lt/min, through a fish aquarium pump with the help of rubber tubing and collected in a covered bucket and re-circulated again. The samples were collected for analysis from the bucket at a regular interval. Fig. 5.7 shows the pictures of actual glass plate solar reactor in operating conditions.

Figure 5.7: glass plate photo reactor

5.3.9 Coated cemented pellets

Reactor design

The small cemented pellets of size 5x5 cm were used as another coating surface for catalyst. The numbers of pellets were placed in glass bowl with 200 ml of stock solution, under solar light. Aeration facility is provided through fish aquarium aerators and the whole process is run without re-circulation. The samples were collected for analysis from a bowl at regular interval. Figure 5.8 shows the cemented beads before coating of catalyst.

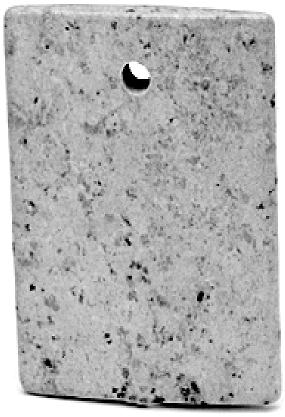


Figure 5.8: cemented beads

Catalyst coating

A 1% aqueous solution of catalyst was prepared and kept for homogenization in sonicator for about 30 minutes. Cemented pellets was then dipped for about an hour in this solution and dried again at 393 K (120 ^{0}c) and kept for 3 hours at final temperature. However a constant rate of temperature increase was maintained at 3^{0}c/min for avoiding the cracking of catalyst layer due to sudden exposure to high temperature.

5.3.10 Coated alginate balls

Reactor design

Sodium Alginate gel was used as another coating material for catalyst. The numbers of spherical coated balls were placed in glass bowl with 200 ml of stock solution, under solar light. Aeration facility is provided through fish aquarium aerators and the whole process is run without re-circulation. The samples were collected for analysis from a bowl at regular interval. Figure 5.9 shows coated alginate balls after the treatment of compound.

Figure 5.9: Coated Sodium Alginate balls

Catalyst coating

A 2% Sodium Alginate gel was prepared by adding 1gm of sodium alginate in 50ml distilled water. A 1% aqueous solution of catalyst was prepared and kept for homogenization in sonicator for about 30 minutes. The sonicated catalyst solution was mixed with alginate gel and with the help of auto pipette small coated balls were developed using Calcium chloride; for the formation and storage of coated alginate balls. The balls are kept in refrigerator for complete binding of catalyst, at the temperature of 3^0c for an hour.

Chapter 6

Results and Discussion

6.1 Compound Characteristics:

The technical grade 2-chloro-4-nitrophenol was taken and analyzed for its various parameters. The values of the various parameters are shown in **(Table 6.1)**

Table 6.1: showing characteristics of 2-chloro-4-nitrophenol

Parameters	Value
pH of compound	4.0
COD of Compound	400 mg/litre
Maximum absorbance	229.5 nm

6.2 Standard curve of 2-chloro-4-nitrophenol

Figure 6.1 shows the standard curve for 2-chloro-4-nitrophenol which is prepared by plotting the absorbance of 2-C-4-NP solution of varying known concentration ranging from 10ppm to 100 ppm at 229.5 nm. From this graph we can calculate unknown concentration for 2-C-4-NP solution. Value of R^2 is 0.997 and slope is 0.0396.

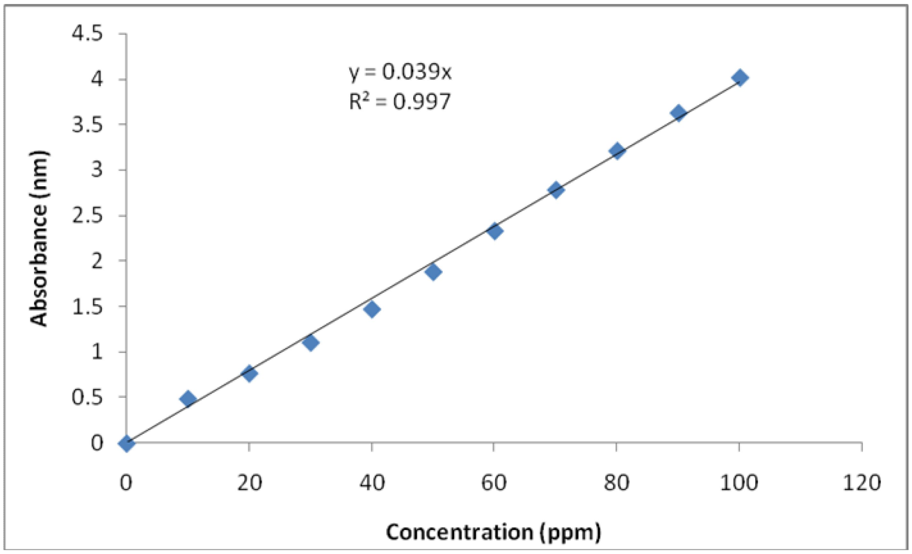


Figure 6.1: Standard curve of 2-chloro 4-nitrophenol

6.3 Preliminary studies

Negligible degradation was found when an aqueous solution of 2-chloro 4-nitrophenol was treated in dark (catalyst only) and in the absence of catalyst (light only). Around 6% degradation was observed in dark and 9% with only artificial light. The reason for the decrease in concentration is basically adsorption of pollutants on the surface of catalyst. An oxidant (H_2O_2) also, individually shows very minuet degradation, which is due to the generation of some OH radicals and oxidant along with UV light cannot create a big difference in degradation. A complete degradation of 2-chloro 4-nitrophenol could only be observed with the simultaneous presence of TiO_2, UV light and oxidant.

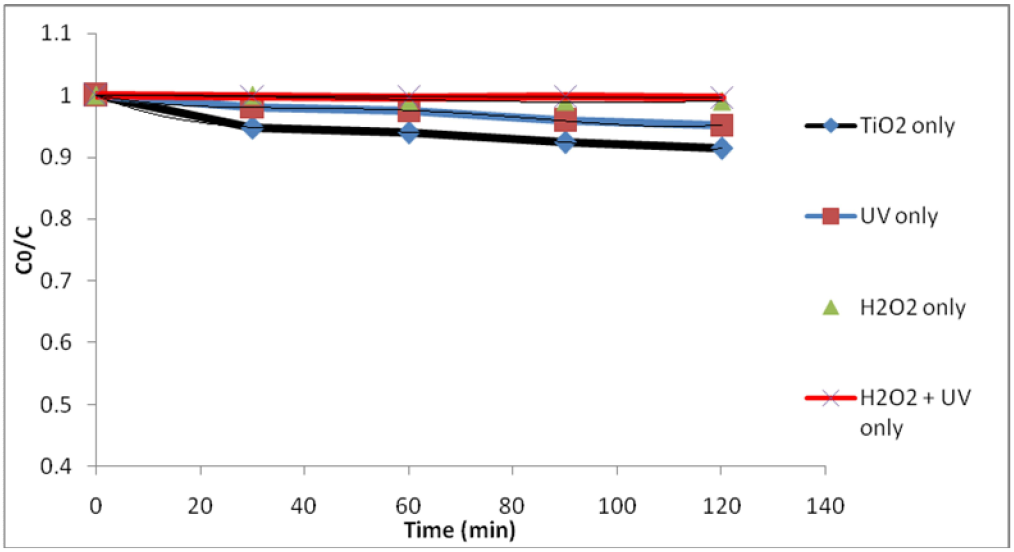


Figure 6.2: Preliminary study of 2-chloro 4-nitrophenol

6.4 Photocatalytic treatment and process optimization

The preliminary studies clearly indicate the need of effective treatment for the complete degradation and mineralization of the compound. So, the efforts are made to treat the raw compound with the help of photocatalysis process. Photocatalytic treatment is affected by the following factors:

- Concentration of the catalyst
- Operating pH of the process
- Concentration of the oxidant added
- Effect of UV intensity

So the Photocatalytic treatment process was optimized for the following factors and these optimized conditions were used for the further actual treatment of the 2-C-4NP. Photocatalytic reactions can usually be described by a pseudo-first order kinetic expression.i.e.

$$-dC/dt = K\ Ct.\ Or$$

$$i.e.\ In\ C_0/Ct = kt$$

Where C_0 and Ct are the concentration of 2C-4-NP at times 0 and t, and k is an apparent reaction rate constant.

Here plot of lnC_0/Ct Vs time was plotted and slope of graph will be apparent reaction rate constant (K).

6.4.1 Concentration of photocatalyst

Photocatalyst used was TiO_2 in varying concentrations ranging from 0.5 g/l to 3.0g/l during the photocatalytic treatment process for optimization of the concentration. The maximum degradation of 73% was achieved with 1g/l concentration of photocatalyst. It was observed that rate of photocatalytic process increase with increase in concentration of the catalyst up to certain limit and then becomes constant and starts to decrease after certain limit as shown in figure 6.3.

The reasons for this decrease in degradation rate are:

- Clustering of catalyst particles at higher concentration and thus causing a decrease in the number of active sites on its free surface.
- Decrease in opacity and increase in scattering of solar UV light by TiO_2 particles at higher concentration and thus leading to interruption in the passage of radiation through the sample solution.

As the concentration of TiO_2 is increased, the number of photons absorbed from UV light and the number of compound molecules absorbed on the surface of catalyst are increased owing to an increase in rate of photocatalytic reaction. Above a certain level, the compound molecules available are not sufficient for the adsorption by the increased number of TiO_2 particles. Hence the increased catalyst amount is not involved in the catalytic activity and the rate does not increase with increase in the amount of catalyst beyond a certain limit. However after certain limit the no. of active sites on the surface of catalyst also decreases due to clustering of TiO_2 particles at higher concentrations.

So an amount of 1g/l of TiO_2 has been taken for the subsequent experiments for the optimization of the operating pH and concentration of oxidant to be added.

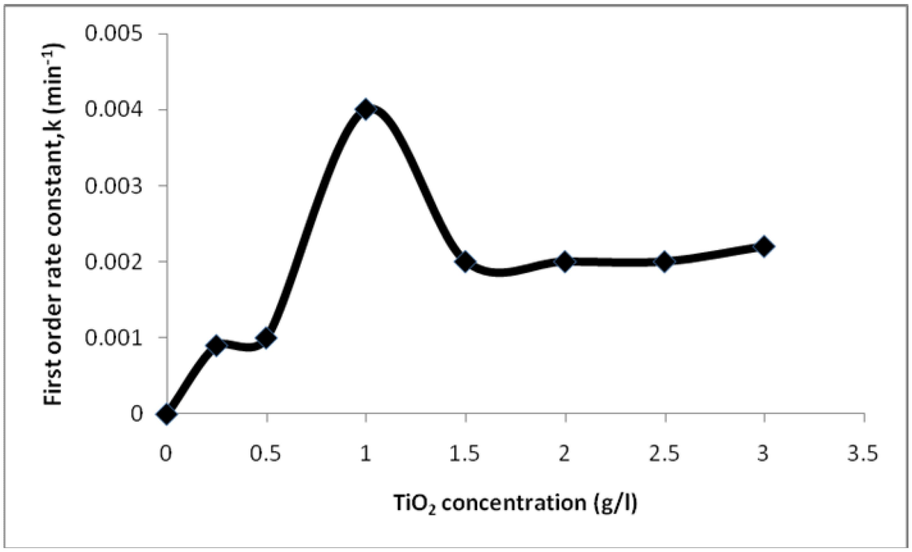


Figure 6.3: optimization of catalyst concentration for the treatment of 2-C 4-NP (C_o=100 mg L^{-I})

6.4.2 Effect of operating pH

The generation of hydroxyl radicals in AOPs is also effected by pH of the solution. Thus pH plays an important role in generation of hydroxyl radicals. So, attempt has been made to study the effect of pH in the photocatalytic treatment of 2-C 4-NP in the pH ranges of 2.5 to 8.5 at optimized catalyst concentration. Figure 30 indicates maximum degradation at pH 4.5, which is the natural pH of 2-C 4-NP.

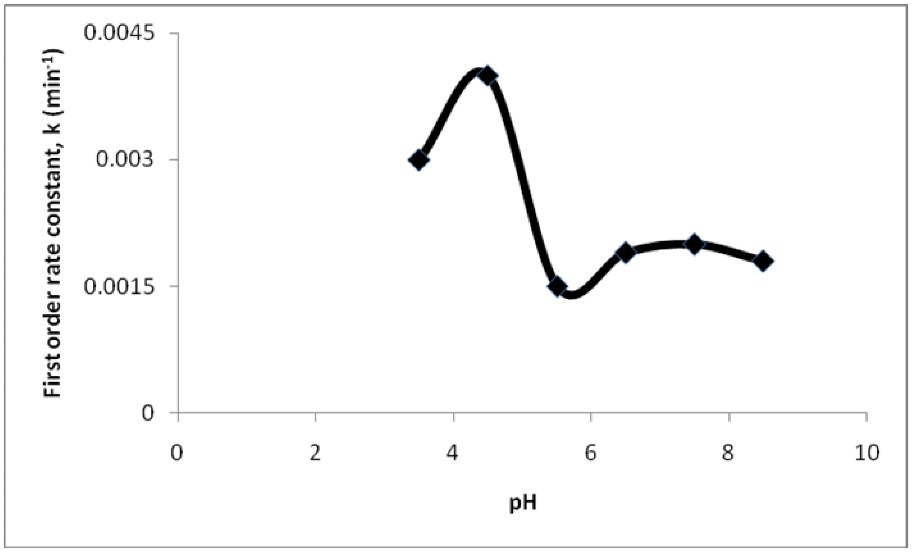


Figure 6.4: Effect of operating pH for the treatment of 2-C 4-NP with 1g/L TiO_2 (C_o=100 mg L^{-1})

According to the literature, the operating pH of process and solution significantly affects catalyst activity, in which charge on the particles, the size of the aggregates formed and the positions of the conduction and valance bonds are included.

In our experiment, maximum degradation was observed at pH 4.5. According to Okamoto et al., (1985), the mechanism for photocatalytic reaction in the presence of titanium dioxide is shown below.

$TiO_2 \rightarrow h^+ + e^-$
$H_2O + h^+ \rightarrow {}^{\cdot}OH + H^+$
$OH^-_{(s)} + h^+ \rightarrow {}^{\cdot}OH$
$O_2 + e^- \rightarrow {}^{\cdot}O^-_2$
${}^{\cdot}O_2^- + H^+ \rightarrow {}^{\cdot}HO_2 \; pK_a = 4.88$
${}^{\cdot}HO_2 + {}^{\cdot}HO_2 \rightarrow H_2O_2 + O_2$
$H_2O_2 + O_2^- \rightarrow {}^{\cdot}OH + OH^- + O_2$
$H_2O_2 \rightarrow 2\,{}^{\cdot}OH$

When pH value is higher than pKa (4.88) for HO_2 radical, the reaction proceeds in the reverse direction. The lack of HO2 radicals makes reaction difficult to proceed. Therefore, the formation of OH free radicals was supplied by the reaction of positive holes with water and OH on the surface of titanium dioxide. Okamoto et al. also found that the formation of OH free radicals being mainly from H_2O_2, which would not favour the decomposition of 2-chloro 4-nitro phenol at a high pH region. For pH value less than 4.88 in, the reaction favours the formation of more ${}^-OH$ free radicals.

6.4.3 Effect of oxidant addition

The addition of other powerful oxidizing species such as H_2O_2 or $K_2S_2O_8$ to TiO_2 suspensions is a well known procedure and in many cases leads to an increase of the rate of photooxidation (Graetzel et al., 1990; Pelizzetti et al., 1991). H_2O_2 is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation (eq.1). It also forms OH radicals according to eq. (2)

$$H_2O_2 + e^- \text{-------->} OH^- + OH^{\cdot} \qquad (1)$$

$$H_2O_2 + O^{2\cdot} \text{--------->} OH^{\cdot} + OH^- + O_2 \qquad (2)$$

In the present study, experiments were conducted with varying the hydrogen peroxide concentration from 0 to 45mM. The best results were obtained when oxidant addition came out to be 7.5mM of sample and have been taken as the optimum amount required for maximum effective treatment of pollutant (figure 6.5). A similar observation shows that the degradation rate increases with increases in addition of H2O2, becomes maximum at certain level and then starts decreasing with further increase in the concentration of H_2O_2. (Davis and Huang, 1990).

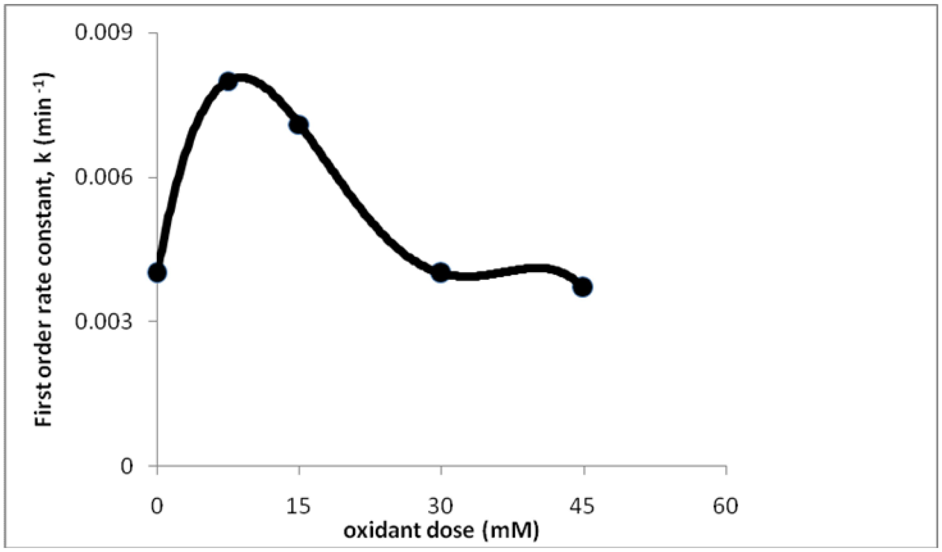


Figure 6.5: Effect of oxidant dose for the treatment of 2-C 4-NP at optimum conditions (C_o=100 mg $L^{-}1$, 1g/L TiO_2 and 4.5pH)

6.4.4 Effect of UV intensity

In the field application of Advance treatment solar energy is always preferred. The intensity of solar light is a variable in nature throughout the year. So the efforts are made to study the effect of UV intensity on photocatalytic treatment of 2-C 4-NP.

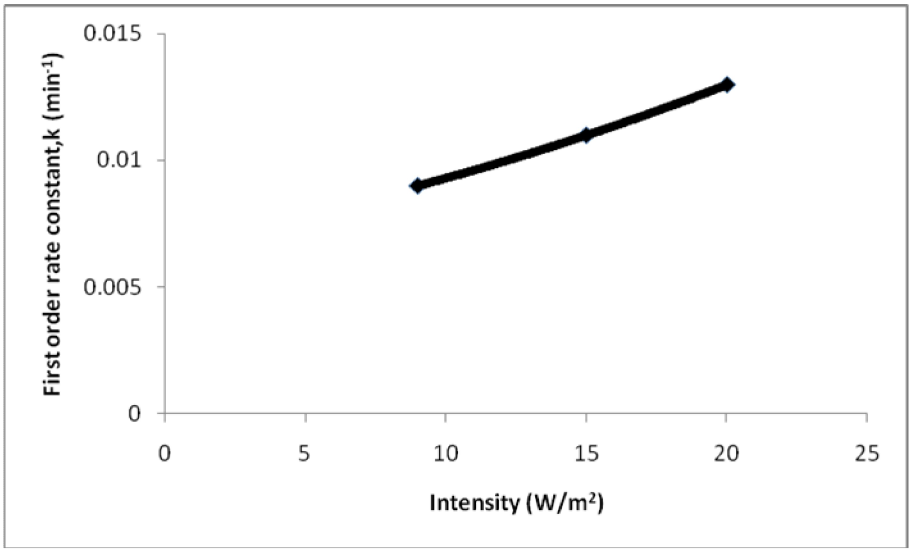


Figure 6.6: Effect of UV intensity at the optimum conditions (C_o=100 mg L^{-1}, 1g/l TiO_2, 4.5 pH, and 7.5mM H_2O_2)

The experiments were conducted with all the optimum conditions in the shallow slurry pond reactor under artificial light at three different intensities of 9, 15 and 20 W/m^2. The degradation rate constant was increases with increase in intensity, and best results were obtained at 20w/m^2 (figure 6.6). Similar studies were done by D. Bahnemann (1999) with three different dyes which show that, at the higher intensity of light irradiation, the enhancement was considerably higher because that the electron–hole formation is predominant and, hence, electron–hole recombination is negligible. However, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the percentage degradation of the dyes.

6.5 Comparison between Artificial and Solar light

From the experiment conducted with all the optimum conditions (1gm/l of TiO_2, 4.5 pH, and 7.5mM H_2O_2) in shallow slurry pond type reactor under artificial UV light, study was done in solar light to seek the commercial applications of the technology. All the experiments were done in the months of April and May between 9.30 am to 5pm to harness maximum solar radiations. Since sunlight is abundantly available natural energy source, its energy can be conveniently exploited for the irradiation of semiconducting materials like TiO_2, ZnO_2 etc. UV irradiation is yet another high energy source for degradation of organic material present in the effluents. The best results were obtained under solar light (89%) as compared to artificial light (80%) after 6 hour of photocatalytic treatment. Figure (6.7) shows the comparison between solar and artificial photocatalytic treatment of 2-C4-NP. Similar kind of study has been reported in literature by S. Shanmuga Priya et al., (2008), which proven solar treatment better, than the UV (artificial) light.

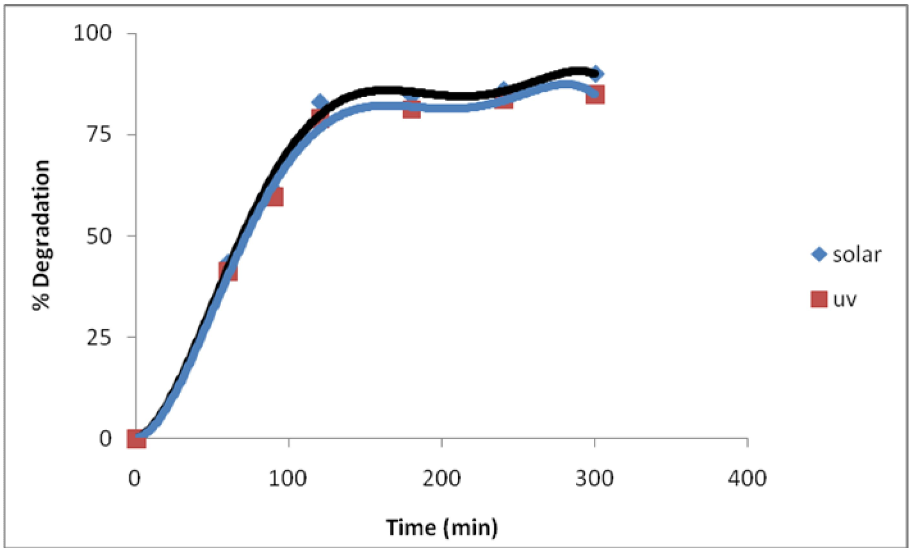


Figure 6.7: Comparison between Artificial and Solar light at the optimum conditions (C_o=100 mg L^{-1},1g/l TiO_2, 4.5 pH, and 7.5mM H_2O_2)

6.6 Effect of initial substrate concentration

The effect of initial concentration of 2-C 4-NP on the percentage degradation was studied by varying the initial concentration from 25 mg/L^{-1} to 200 mg/ L^{-1} with all the optimum conditions. The result shows (figure 6.8) that the rate of reaction is increasing upto a certain concentration of raw compound, after that depletion take place. According to Evgenidou E. et al., (2005) it is obvious that the rate increases with the increase of the initial concentration of dimethoate until it reaches a saturation value at high concentration of the insecticide.

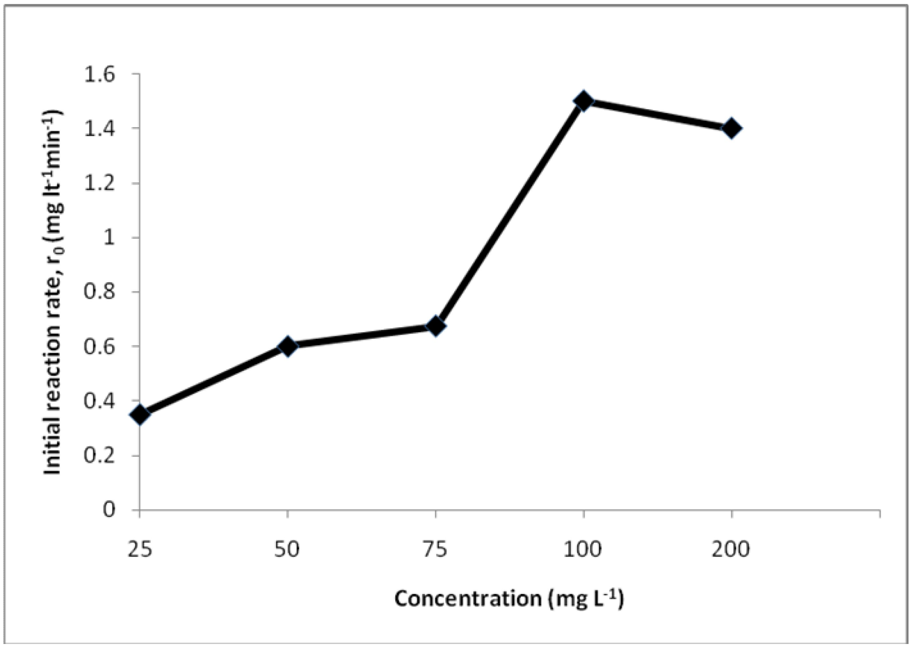


Figure 6.8: Effect of substrate concentration at the optimum conditions (C_o=100 mg L^{-1},1g/l TiO_2, 4.5 pH, and 7.5mM H_2O_2)

6.7 Fixed Bed Photocatalysis

Since the suspended TiO_2 powder employs free contact with UV radiation in a photoreactor system, it can generally achieve better efficiency then the immobilized TiO_2 catalyst. However, the separation and reuse of this catalyst powder from treated water often limits its application in practice. To preclude the separation procedure, the immobilization of the TiO_2 catalyst on certain supporting materials such as glass fiber, or stainless steel has been frequently adopted as reviewed by Byrne et al., (1998).

The experiment performed with fixed bed photocatalytic reactor show that degradation is low in this case as compared to that observed in case of shallow pond slurry type reactor at lab scale. Many reasons may be attributed to this observation, as there is much less contact of catalyst with the organic pollutants than in case of slurry. Moreover flow velocity also influences the rate of reaction; it should not be too high or too low. But it is kept optimum for proper contact time of catalyst with the organic pollutant. No doubt, it takes longer time for the same extent of degradation as in slurry form, but it has no drawback like arranging for the removal of catalyst from the treated effluent with the help of filtration or any other method and so making the process cheaper. Rachel and Subrahmanyam (2002) and Shephered et al., (2002) has observed a significant loss in the contact area between the immobilized photocatalyst and a light source limits its efficiency in the photocatalytic degradation of the organic substrates.

6.7.1 Glass Plate Solar Reactor

The material required for the fixing of the catalyst is always a major challenge for the scientists working in this area. Lesser degradation rates, mass transfer limitations, catalyst film stability etc. are some parameters which actually restrict the pilot and industrial scale applications of this technology. Moreover to best of our knowledge, no studies have been done in literature for the degradation of 2C-4NP using fixed bed. In this context efforts have been done using glass plate (method and design discussed in material and method) for fixing the catalyst. The experiment was performed using glass plate solar reactor with all the optimum conditions achieved in slurry type reactor. The result shows (figure 6.9) 70% degradation was obtained after 14 hrs irradiation.

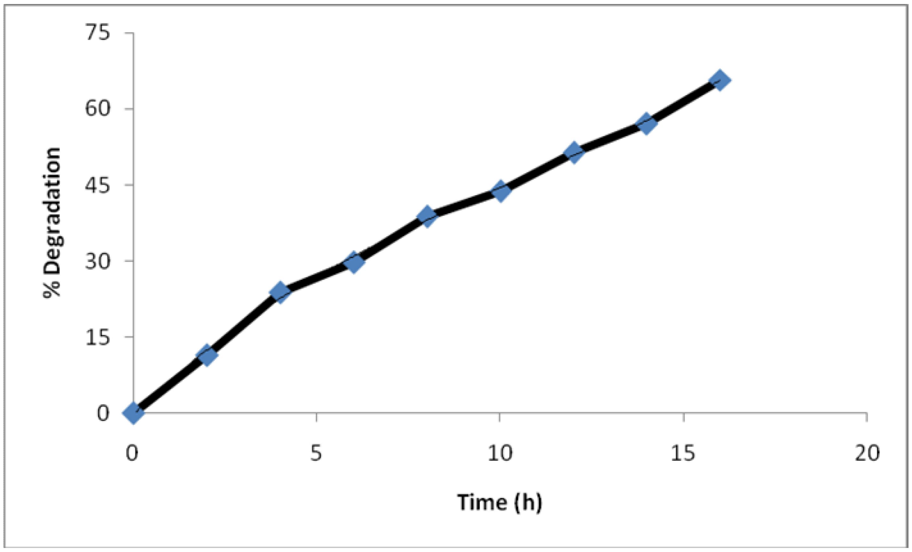


Figure 6.9: Degradation by glass plate solar reactor at the optimum conditions (C_o=100 mg L^1, 1g/l TiO_2, 4.5 pH, and 7.5mM H_2O_2)

6.7.2 Immobilized Cemented Beads

Photocatalytic degradation study has been undertaken using cement beads immobilized with TiO_2. Many studies have been cited in the literature where cement bed has been used for catalyst fixing in degradation of pollutants [Zayani G. et al., 2009]. But studies using cement beads for the degradation of 2-C-4-NP has not been reported yet. Thus the experiment was performed using suitable number of Immobilized Cemented Beads under artificial light as well as sunlight under all the optimum conditions achieved in shallow slurry pond reactor.

65% degradation was observed in artificial UV light and almost similar in sunlight (Figure 6.10).

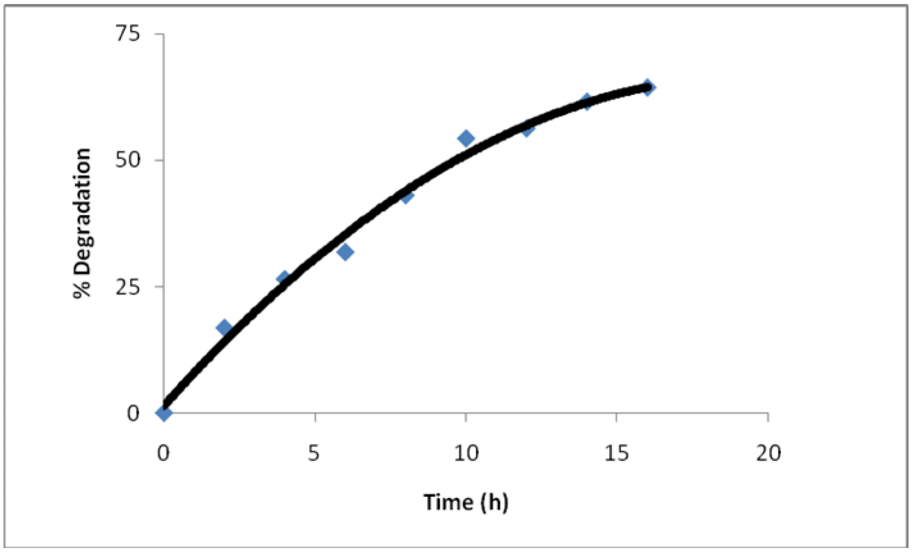


Figure 6.10: Degradation by coated cemented beads at the optimum conditions (C_o=100 mgL^{-1},1g/l TiO_2, 4.5 pH, and 7.5mM H_2O_2)

6.7.3 Sodium Alginate Balls

In another study, an attempt is made to physically entrap the catalyst in a gel. To best of our literature search, not a single paper has been published using physically entrapped TiO_2 beads. Although we were not able to do many variations in this study, yet simple entrapment in sodium alginate gel was studied for the degradation of the 2-C-4NP. The experiment was performed using fixed number of sodium alginate balls in shallow slurry pond type reactor under artificial light with all the optimum conditions. Figure (6.11) shows 60% degradation of 2-C4-NP by sodium alginate balls.

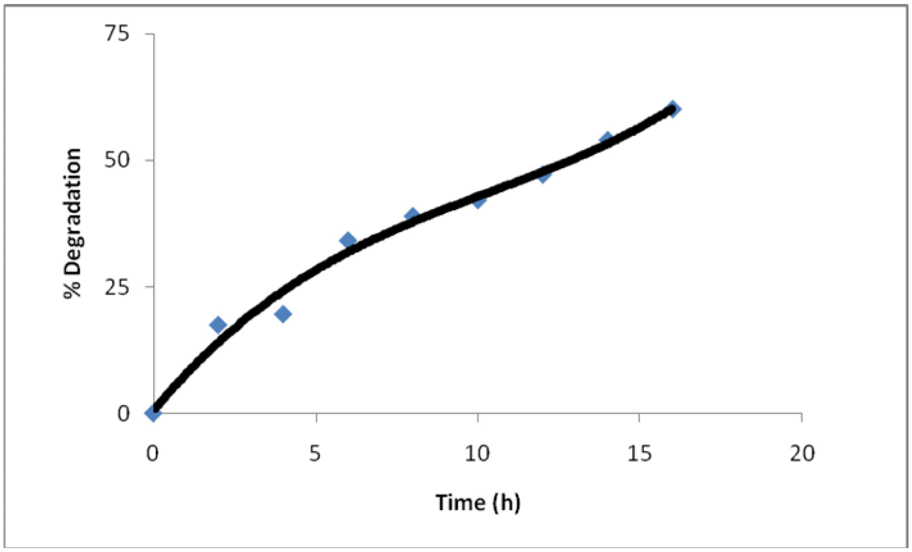


Figure 6.11: Degradation by sodium alginate balls at the optimum conditions (C_o=100 mg L^{-1},1g/l TiO_2, 4.5 pH, and 7.5mM H_2O_2)

6.8 Mineralization studies

A complete degradation of an organic molecule by photocatalysis normally leads to the conversion of all the carbon atoms to gaseous CO_2, and the heteroatoms into inorganic anions that remain in solution. In order to study the mineralization of 2-C 4-NP, the COD reduction along with the nitrate ions generation was estimated. The 90% reduction in COD along with the generation of nitrate ions (99%) confirms the complete mineralization of compound under study during 5 h of photocatalytic treatment.

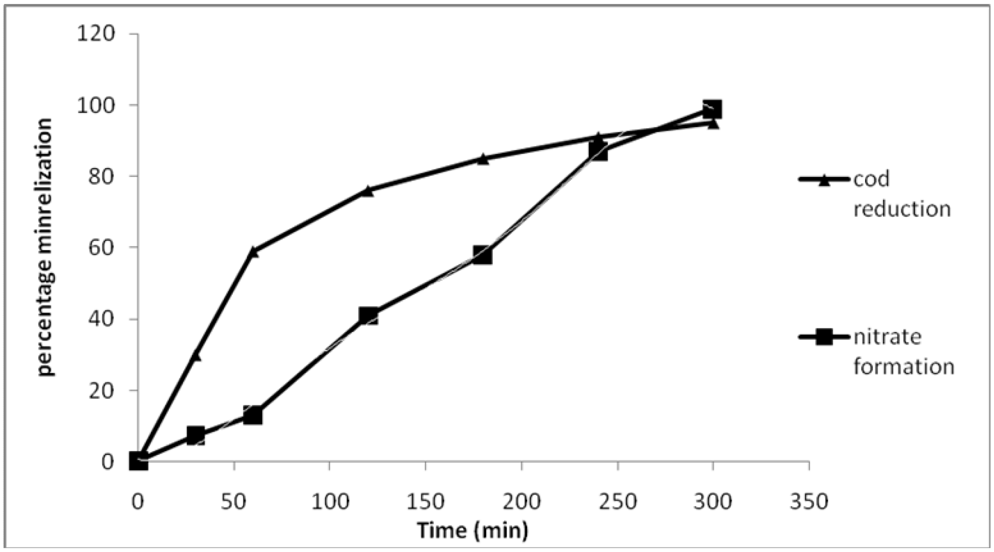


Figure 6.12: Mineralization of 2-C 4-NP at the optimum conditions (C_o=100 mg L^{-1},1g/l TiO_2, 4.5pH, and 7.5mM H_2O_2)

Chapter 7

Conclusion

Most studies related to photocatalytic degradation of organic pollutants have been carried using suspension of powdered TiO_2; however the disadvantage of this is an increase in the overall capital and running cost of the plant due to filtration of the catalyst.

Therefore attempts have been made to immobilize the catalyst on different supports, such as glass, cement beads and sodium alginate balls; and solar irradiation was used for complete mineralization of raw compound (2 Chloro 4 Nitrophenol). Fixed-bed photocatalytic degradation of 2-C 4-NP, using TiO_2 (Degussa P25) photocatalyst depends on the amount of catalyst, oxidant dose, pH and solar light intensity. Degradation observed was 89%, 70%, 65% and 60% under suspension solar-photocatalytic, glass-plate solar reactor, coated cemented beads and immobilized sodium alginate ball; respectively at optimized conditions i.e. 4.5 pH, catalyst concentration of 1 g/l and oxidant dose of 7.5mM/200ml. The dip and coating method was used for the catalyst immobilization on the glass and cemented beads, whereas in other case, physical entrapment of the catalyst slurry in the gel was used. Approximately 90% reduction in COD confirms the mineralization of the compound under study. This process has proved its superiority to other conventional methods of waste water treatment, in the presence of biorecalcitrant compounds.

The future aspects of this technology is very viable and cost effective as the cost of construction is eliminated by using cheap and discarded material for the of coating catalyst and energy cost is eliminated by solar energy. The application of this technology is to use these kind of fixed materials for the degradation of biorecalcitrant compounds inside the shallow pond type slurry reactor specially for the region receiving strong sunlight throughout the year.

Though solar irradiation can bring better efficiency in the degradation of raw compound, solar energy will emerge as an alternative cost effective light source because of its abundance and non-hazardous nature. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries intense sunlight is available throughout the years and, hence, it could be effectively used for photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation, sunlight would be the ultimate source. Moreover there is no material deterioration in case that sunlight is used as a radiation source.

Hence, this technique may be a viable one for treatment of large volume of wastewater of low concentration.

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