PHOTOCATALYTIC DEGRADATION OF PROCION YELLOW DYE

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DECLARATION

I hereby declare that the work embodied in dissertation entitled **"Photocatalytic degradation of Procion Yellow Dye"** is original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

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CERTIFICATE

This is to certify that the dissertation entitled "**Photocatalytic degradation of Procion Yellow Dye**" is an authentic work carried out by Pradeep Kumar, student of M.Tech (Env. Sc. & Technology) Thapar University Patiala, during year 2009-2010, in partial fulfillment for the award of the degree of Master of Technology & 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

Since the beginning of industrialization, the variety and quantity of pollutants emitted into the environment has steadily increased. While the rates of development and waste production are not likely to diminish, efforts to control and dispose of wastes are rising. Textile wastewaters consist of an amalgam of dyes, surfactants, and additives that are acquired throughout the application processes. Because of the extensive variation in type and distribution of chemicals found in the effluents, no single, comprehensive method of treatment has been developed. Studies have shown some chemical and physical techniques (coagulation, ultra filtration, and reverse osmosis) in effectively removing certain dyes from wastewater however, these systems merely transfer the dye from one form of waste to another (e.g. liquid to solid), and therefore cannot be considered as a complete treatment of the waste. An alternative mode of pollutant treatment is photocatalytic oxidation. This advanced oxidation process entails illuminating a photocatalyst (typically titanium dioxide, TiO_2) with a particular wavelength of light to generate radicals; these radicals will subsequently oxidize the organic pollutants to CO_2 and H_2O. These processes frequently include the addition of oxidizing agents in the presence of a Catalyst or UV light. These types of processes are collectively called as advanced oxidation processes (AOP's). The principal mechanism of AOP's function is the generation of highly reactive free radicals. TiO_2 has been demonstrated to be excellent catalyst and its behavior is well documented in the literature.

Photo degradation of Procion yellow dye was performed in specially designed reaction vessel in the photo reactor equipped with UV tubes and constant stirring of solution was ensured at constant temperature. The comparing study of TiO_2 & ZnO as a catalyst for the degradation of Procion Yellow Dye was performed. Experiments were performed in slurry mode in both UV and solar light at optimized processes parameter. Various parameters like catalyst dose, pH, effect of UV/solar, initially dye concentration was varied and their effects have been analyzed.

Procion yellow dye (100ppm) was degraded in the presence of TiO_2 dose (0.5g/l), at natural pH with UV and Solar light. 83.60% degradation was achieved in UV light & 76.8% degradation was achieved in solar light at the optimized parameter.

Titainum dioxide and zinc oxide could be used powerfully in photocatalytic degredation of PY Dye solution. Although ZnO is the most efficient catalyst but it has the disadvantage of undergoing photocorrosion under illumination in acidic conditions and high cost. In the case of Zinc Oxide, ZnO dose was optimized to be 0.25g/l, at pH of 8.0 with UV light., 92.01% degradation was achieved in UV light where as 87.92% degradation was achieved in solar light under the optimized parameters. While the treatment of Procion yellow dye with TiO_2 catalyst yields COD reduction from 2000 to 1000 mg/l in UV light and 2000mg/l to 1200mg/l in solar light was after 3.5 hrs. And in the presence of ZnO, COD reduction from 2000 to 800 mg/l in UV light and 2000mg/l to 1000mg/l in solar was observed after 75 min. So the reaction time for degradation of dye with ZnO is quite less as compared to $TiO_{2.}$

The results of photo degradation of Procion yellow dye showed that heterogeneous photo catalytic could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater. The investigations demonstrate the importance of selecting the optimal degradation parameters for practical applications of this operation. The results depict that solar light can be effectively used for the degradation of Procion yellow dye and this will help in the economic viability of the process at industrial scale.

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CHAPTER 1

1 INTRODUCTION

Comprising over 70% of the Earth's surface, water is undoubtedly the most precious natural resource that exists on our planet. Without the seemingly invaluable compound comprised of hydrogen and oxygen, life on Earth would be non-existent: it is essential for everything on our planet to grow and prosper. Although we as humans recognize this fact, we disregard it by polluting our rivers, lakes, and oceans. Subsequently, we are slowly but surely harming our planet to the point where organisms are dying at a very alarming rate. In addition to innocent organisms dying off, our drinking water has become greatly affected as is our ability to use water for recreational purposes. In order to combat water pollution, we must understand the problems and become part of the solution.

1.1 Point and non-point sources

According to the American College Dictionary, pollution is defined as: "to make foul or unclean; dirty." Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. When it is unfit for its intended use, water is considered polluted. Two types of water pollutants exist: point source and non-point source. Point sources of pollution occur when harmful substances are emitted directly into a body of water. A non-point source delivers pollutants indirectly through environmental changes. An example of this type of water pollution is when fertilizer from a field is carried into a stream by rain, in the form of run-off which in turn affects aquatic life. The technology exists for point sources of pollution to be monitored and regulated, although political factors may complicate matters (Wilcock, 1988). Nonpoint sources are much more difficult to control. Pollution arising from nonpoint sources accounts for a majority of the contaminants in streams and lakes.

1.2 Causes of pollution

Many causes of pollution including sewage and fertilizers contain nutrients such as nitrates and phosphates. In excess levels, nutrients over stimulate the growth of aquatic plants and algae. Excessive growth of these types of organisms consequently clogs our water ways, use up dissolved oxygen as they decompose, and block light to deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiration ability or fish and other invertebrates that reside in water. Pollution is also caused when silt and other suspended solids, such as soil, wash-off plowed fields, construction and logging sites, urban areas, and eroded river banks when it rains (Street et al., 1925). Under natural conditions, lakes, rivers, and other water bodies undergo Eutrophication, an aging process that slowly fills in the water body with sediment and organic matter. When these sediments enter various bodies of water, fish respiration becomes impaired, plant productivity and water depth become reduced, and aquatic organisms and their environments become suffocated. Pollution in the form of organic material enters waterways in many different forms as sewage, as leaves and grass clippings, or as runoff from livestock feedlots and pastures. When natural bacteria and protozoan in the water break down this organic material, they begin to use up the oxygen dissolved in the water. Many types of fish and bottom-dwelling animals cannot survive when levels of dissolved oxygen drop below two to five parts per million. When this occurs, it kills aquatic organisms in large numbers which leads to disruptions in the food chain.

1.3 Additional forms of water pollution

Three last forms of water pollution exist in the forms of petroleum, radioactive substances, and heat. Petroleum often pollutes water bodies in the form of oil, resulting from oil spills. The Exxon Valdez is an example of this type of water pollution. These large-scale accidental discharges of petroleum are an important cause of pollution along shore lines. Besides the super tankers, off-shore drilling operations contribute a large share of pollution. One estimate is that one ton of oil is spilled for every million tons of oil transported. On the other hand, the number of organic compounds have been synthesized since the turn of the century now exceeds, half a million, and some 10,000 new compound are added each year, as results, many of these compounds are now found in the wastewater from most industrial (Brown and Barnwell, 1985). Radioactive substances are produced in the form of waste from nuclear power plants, and from the industrial, medical, and scientific use of radioactive materials. Specific forms of waste are uranium and thorium mining and refining. The last form of water pollution is heat. Heat is a pollutant because increased temperatures result in the deaths of many aquatic organisms. These decreases in temperatures are caused when a discharge of cooling water by factories and power plants occurs.

1.4 Classifying water pollution

The major sources of water pollution can be classified as municipal, industrial, and agricultural. Municipal water pollution consists of wastewater from homes and commercial establishments. For many years, the main goal of treating municipal wastewater was simply to reduce its content of suspended solids, oxygen-demanding materials, dissolved inorganic compounds, and harmful bacteria. In recent years, however, more stress has been placed on improving means of disposal of the solid residues from the municipal treatment processes. The basic methods of treating municipal wastewater fall into three stages: primary treatment, including grit removal, screening, grinding, and sedimentation; secondary treatment, which entails oxidation of dissolved organic matter by means of using biologically active sludge, which is then filtered off; and tertiary treatment, in which advanced biological methods of nitrogen removal and chemical and physical methods such as granular filtration and activated carbon absorption are employed. The handling and disposal of solid residues can account for 25 to 50 percent of the capital and operational costs of a treatment plant. The characteristics of industrial wastewaters can differ considerably both within and among industries. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic and organic substances. Three options are available in controlling industrial wastewater (Thomas 1982). Control can take place at the point of generation in the plant; wastewater can be pretreated for discharge to municipal treatment sources; or wastewater can be treated completely at the plant and either reused or discharged directly into receiving waters.

1.5 Constituents found in wastewater

Wastewater characterized in term of its physical, chemical and biological composition, the principle physical, chemical and biological constituents of wastewater and their sources are reported in table 1.1. It should be noted that many of the parameters listed in table 1.1 are interrelated. For example, temperature, physical property, affects both chemical and biological activity in the wastewater and the amount of gases dissolve in the wastewater.

Table 1.1: Physical, chemical, and biological characteristics of wastewater and their sources (Metcalf and Eddy, 1985)

Characteristic	Source
Physical properties	
Color	Domestic and industrial waste, natural decay of organic
Odor	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes Soil erosion inflow/infiltration
Temperature	Domestics and industrial wastes
Chemical constituents	
Organic	Domestic, commercial, and industrial wastes
Carbohydrate	Domestic, commercial, and industrial wastes
Fats, oil and grease	Agricultural wastes
Pesticides	Industrial wastes
Phenols	Domestic, commercial, and industrial wastes
Chlorides	Domestic wastes, domestic water supply, groundwater infiltration
Heavy metals	Industrial wastes
Nitrogen	Domestic, commercial, and industrial wastes
Sulfur	Domestic water supply; domestic, commercial, and industrial wastes
Hydrogen sulfide	Domestic, commercial, and industrial wastes
Methane	Domestic, commercial, and industrial wastes
Oxygen	Domestic water supply, surface-water infiltration
Biological constituents	
Animals	Open watercourses and treatment plant
Plants	Open watercourses and treatment plant
Eubacteria	Domestic wastes. Surface-water infiltration, treatment plants
Viruses	Domestic wastes

1.6 Contaminant of concern in wastewater treatment

The important contaminants of concern in wastewater treatment are listed in table 1.2. Secondary treatment standards for wastewater are concerned with the removal of biodegradable organic, suspended solids, and pathogens. Many of the more stringent standards that have been developed recently deal with the removal of nutrients and priority pollutants (Levine et al., 1985). Recently, The European Union made out a list of dangerous compounds (see Table 1.3); considered as contaminants, to which constantly new substances are added ("black list" of the E.U.,)

Table 1.2: Important contaminants of concern in wastewater treatment:

Contaminants	Reasons for importance
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharge in the aquatic environment
Biodegradable organic	measured most commonly in terms of BOD (Biological oxygen demand) and COD (chemical oxygen demand) if discharged untreated to the environment, their biological stabilization can lead to the depletion of natural oxygen resources and to the development of septic conditions
Pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater
Priority pollutants	Organic and inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagencity, teratogenicity, or high acute toxicity. Many of these are found in wastewater
Refractory organics	These organics tend to resist congenital methods of wastewater treatment. Typical examples include surfactant, phenols, and agricultural pesticides
Heavy metals	Heavy metals are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be used
Dissolved inorganic	Inorganic constituents such as calcium. Sodium, and sulphate are added to the original domestic water supply as a result of water use and may be have to be removed if the wastewater is to be reused

Table 1.3: Black list of chemicals substances selected by the E.U. (Harrison, 1992)

Group	Included substances
Chloride hydrocarbons	Aldrin, dieldrin, chlorobenzene, dichlorobenzene, chloronaphthalene, chloroprene, chloropropene, chlorotoluene, endosulfane, endrin, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclo-hexane, hexachloroethane, PCBs, tetrachlorobenzene, trichlorobenzene.
Chlorophenol	Monochlorophenol, 2,4-dichlorophenol, 2-amino-4-chlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, trichlorophenol
Chloroanilines and Nitrobenzenes	Monochloroanilines, 1-chloro-2,4-dinitrobenzene, dichloroaniline, 4-chloro-2- Nitrobenzene, chloronitrobenzene, chloronitrotoluene, dichloronitrobenzene.
Polycyclic Aromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene, Dichloromethane, dichloropropane, dichloropropanol, dichloropropene, ethylbenzene, toluene, tetrachloroethylene, trichloroethane, trichloroethylene.

Phenols have been widely used in many industrial processes, as synthesis intermediates or as raw materials in the manufacturing of pesticides, insecticides, wood preservatives, petroleum refining and petrochemicals, pharmaceuticals, paint and dye industries, organic chemicals manufacturing and so forth. Because of the great diversity of their origins, they have a great ubiquity and can be found not only in industrial wastewaters but also in soils and surface and ground waters, as a consequence of their release in industrial effluents or improper waste disposal practices and accidental leakages.

Textile Wastewater processing is one of the most important industries in the world and it employs a variety of chemicals, depending on the nature of the raw material and product. Some of these chemicals are different types of enzymes, detergents, dyes, acids, sodas and salts. The discharge of wastewaters that contains high concentration of reactive dyes is a well-known problem associated with dyestuff activities. The effluents of textile dyeing processes are intensely colored and contaminated with high concentration of dyestuff compounds such as suspended and dissolved salts and much other recalcitrant material. If these effluents are improperly treated, they will pose bad threats to all species on the earth because of the hydrolysis of the pollutants in the wastewater can produce a great deal of toxic products. (Jun Wang et. al 2005)

Dyes constitute a group of organic substances that use in different coloring processing; azoic dyes are the largest chemical class of dyes used regularly for textile and paper printing dyeing (Philippe et al. 1998). Since they are persistent and highly soluble in water, reactive dyes are the most important groups in cellulose dyeing (cotton, polyesters). Other dyes with different characteristic are used for other type of applications; Acid dyes are commonly used in dying polyamide fibers (Nylanthrene dyes are ideally suited to polyamide 6 or 6.6. dyeing).

1.7 Environmental considerations of dye pollution

Dyes are introduced into the environment as a result of several man-made activities. Nowadays, there are more than 5000 commercial dye products, most of these dyes used in textile industry. Thus, this industry is considered as one of the major resource of highly polluted wastewater (Brown et al. (19939)). Fixation rate of a specific dye may vary according to functional groups used to fabricate such a kind of dye. In general more than 40% of initial dye mass remains in the dye bath, and hence its wastewater highly contaminated (Galindo et al., 2001). Modern commercial dyes are very stabile in water solution and they contain high composition ratio of aromatic rings. Thus, it was believed that theses dyes molecule are non-biodegradable and some of them are toxic to bacteria, Some studies using activated sludge suggest that bio-transformation is slow for water-soluble dyes (yoo et al., 2002). Reactive dyes have been reported to go through the biological treatment systems without being removed (Hu et al., 1999)

Table 1.4 some important industries & their principal effluents

Sr. no	**Industry**	**Principal effluent**
1	Bleaching	Sulphite, free chlorine.
2	Breweries	Mineral acid, sugar.
3	Chemical	Phenol, mineral acid, organic acids, nitro compound.
4	Dairies	Sugar.
5	Distilleries	Organic acid.
6	Dyeing	Tartaric acid.
7	Dyes	Phenolic compound.
8	Laundries	Alkalies, fat, oils, free chlorine.
9	Paper	Free chlorine.
10	Textile	Mineral acids, fats, oils, greases.
11	Pesticides	Dichlorodiethylether (DCDE)
12	Pharmaceutical	Dichlorodiethylether (DCDE)
13	Petrochemical	Hydrocarbon
14	Synthetic resin	Formaldehyde & phenol
15	Explosive	aromatic nitro compound

1.8 Objective of present study

Main objective of the study was to degrade a model compound Procion yellow dye (commercial dye) which is a persistent non biodegradable pollutant and cannot be treated by conventional treatment processes. The photocatalytic oxidation of Procion yellow dye which is present in industrial wastewater is the subject of this research. The study was undertaken with the following objectives:

- Photocatalytic treatment of procion yellow dye
- Effect of variables on degradation efficiency and its optimization
- Comparison of different catalyst activity.

CHAPTER 2

2. CONVENTIONAL TREATMENT TECHNOLOGY

The treatments processes of different types of effluents to be used must guarantee the elimination of the pollutant in order to reach the strict authorized levels for the discharge of these effluents. The levels of pollutants allowed in discharge waters, are directly related with the type of present pollutant present in the effluent. In general, the elimination of organic pollutants in aqueous solution need one or various basic treatment techniques *(Naresh N. Mahamuni et. al 2006),* many processes such as membrane separation, wet air oxidation, radiolysis, Fenton oxidation, photo catalytic oxidation, electrochemical oxidation, ozonation, per oxidation and sonication had been used for the degradation of organic compounds to the required low levels. These processes had been used alone or in combination with other processes to achieve the aim. But all these processes have their inherent limitations such as low rates of degradation, or lower mineralization or high costs of operation or severe operating conditions, etc.

Conventional wastewater treatment methods such as Coagulation/Flocculation, adsorption and biological treatment, chlorination, membrane separation etc. do not involve chemical transformations and generally transfer waste component from one phase to another, thus causing secondary loading of environment and waste disposal problem (*Jian-Hui Sun et. al 2006)*. Biological methods are amenable only for biodegradable pollutants as in the case of domestic waste water and industrial effluent in a limited ways.

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Depending upon waste water characteristics, waste water treatment methods should be used.

2.1 Wastewater treatment

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Depending upon waste water characteristics, waste water treatment methods should be used. There are no holidays for wastewater treatment, and most plants operate 24 hours per day every day of the week. Wastewater treatment plants operate at a critical point of the water cycle, helping nature defend water from excessive pollution. Most treatment plants have primary treatment (physical removal of floatable and settle able solids) and secondary treatment (the biological removal of dissolved solids). Generally in wastewater treatment the following steps are:

1. Preliminary treatment
2. Primary treatment
3. Secondary treatment
4. Tertiary treatment

2.1.1 Preliminary Treatment

The objective of preliminary treatment is the removal of coarse solids and other large materials often found in raw wastewater. Removal of these materials is necessary to enhance the operation and maintenance of subsequent treatment units. Preliminary treatment operations typically include coarse screening, grit removal and, in some cases, comminution of large objects. In grit chambers, the velocity of the water through the chamber is maintained sufficiently high, or air is used, so as to prevent the settling of most organic solids. Comminutors are sometimes adopted to supplement coarse screening and serve to reduce the size of large particles so that they will be removed in the form of sludge in subsequent treatment processes. Flow measurement devices, often standing-wave flumes, are always included at the preliminary treatment stage.

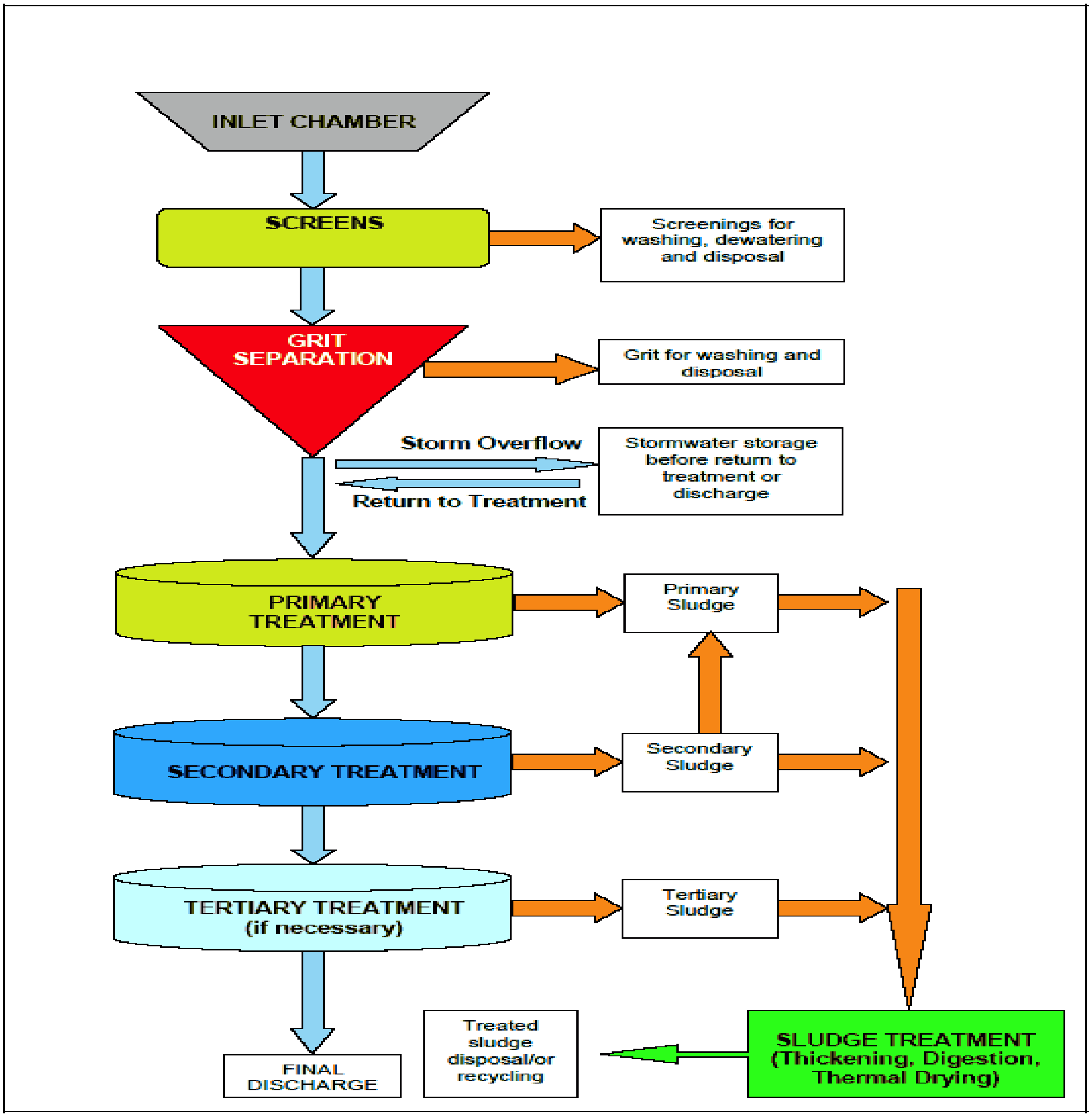

Fig-2.1 Wastewater Treatment

2.1.2 Primary treatment

The objective of primary treatment is the removal of settleable organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming. Approximately 25 to 50% of the incoming biochemical oxygen demand (BOD_5), 50 to 70% of the total suspended solids (SS), and 65% of the oil and grease are removed during primary treatment. The effluent from primary sedimentation units is referred to as primary effluent.

2.1.3 Secondary treatment

The objective of secondary treatment is the further treatment of the effluent from primary treatment to remove the residual organics and suspended solids. In most cases, secondary treatment follows primary treatment and involves the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aerobic biological treatment is performed in the presence of oxygen by aerobic microorganisms that metabolize the organic matter in the wastewater, thereby producing more microorganisms and inorganic end-products (principally CO_2, NH_3, and H_2O). Several aerobic biological processes are used for secondary treatment differing primarily in the manner in which oxygen is supplied to the microorganisms and in the rate at which organisms metabolize the organic matter.

The microorganisms must be separated from the treated wastewater by sedimentation to produce clarified secondary effluent. The sedimentation tanks used in secondary treatment. The biological solids removed during secondary sedimentation, called secondary or biological sludge, are normally combined with primary sludge for sludge processing. Common high-rate processes include the activated sludge processes, trickling filters or biofilters, oxidation ditches, and rotating biological contactors (RBC). A combination of two of these processes in series (e.g., biofilter followed by activated sludge) is sometimes used to treat municipal wastewater containing a high concentration of organic material from industrial sources.

Activated Sludge

In the activated sludge process, the dispersed-growth reactor is an aeration tank or basin containing a suspension of the wastewater and microorganisms, the mixed liquor. The contents of the aeration tank are mixed vigorously by aeration devices which also supply oxygen to the biological suspension. Aeration devices commonly used include submerged diffusers that release compressed air and mechanical surface aerators that introduce air by agitating the liquid surface. Hydraulic retention time in the aeration tanks usually ranges from 3 to 8 hours but can be higher with high BOD_5 wastewaters. Following the aeration step, the microorganisms are separated from the liquid by sedimentation and the clarified liquid is secondary effluent. A portion of the biological sludge is recycled to the aeration basin to maintain a high mixed-liquor

Suspended solids (MLSS) level. The remainder is removed from the process and sent to sludge processing to maintain a relatively constant concentration of microorganisms in the system.

Trickling Filters

A trickling filter or biofilter consists of a basin or tower filled with support media such as stones, plastic shapes, or wooden slats. Wastewater is applied intermittently, or sometimes continuously, over the media. Microorganisms become attached to the media and form a biological layer or fixed film. Organic matter in the wastewater diffuses into the film, where it is metabolized. Oxygen is normally supplied to the film by the natural flow of air either up or down through the media, depending on the relative temperatures of the wastewater and ambient air. Forced air can also be supplied by blowers but this is rarely necessary. The thickness of the biofilm increases as new organisms grow. Periodically, portions of the film 'slough off the media. The sloughed material is separated from the liquid in a secondary clarifier and discharged to sludge processing. Clarified liquid from the secondary clarifier is the secondary effluent and a portion is often recycled to the biofilter to improve hydraulic distribution of the wastewater over the filter.

Rotating Biological Contactors

Rotating biological contactors (RBCs) are fixed-film reactors similar to biofilters in that organisms are attached to support media. In the case of the RBC, the support media are slowly rotating discs that are partially submerged in flowing wastewater in the reactor. Oxygen is supplied to the attached biofilm from the air when the film is out of the water and from the liquid when submerged, since oxygen is transferred to the wastewater by surface turbulence created by the discs' rotation. Sloughed pieces of biofilm are removed in the same manner described for biofilters. High-rate biological treatment processes, in combination with primary sedimentation, typically remove 85 % of the BOD_5 and SS originally present in the raw wastewater and some of the heavy metals. Activated sludge generally produces an effluent of slightly higher quality, in terms of these constituents, than biofilters or RBCs.

2.1.4 Tertiary / advanced treatment

Tertiary treatment is employed when specific wastewater constituents which cannot be removed by secondary treatment must be removed. Individual treatment processes are necessary to remove nitrogen, phosphorus, additional suspended solids, refractory organics, and heavy metals and dissolved solids. Because advanced treatment usually follows high-rate secondary treatment. However, advanced treatment processes are sometimes combined with primary or secondary treatment (e.g., chemical addition to primary clarifiers or aeration basins to remove phosphorus) or used in place of secondary treatment (e.g., overland flow treatment of primary effluent).

The removal of contaminant from industrial waste water tertiary method is used. These are Incineration, Air stripping, Adsorption processes, Wet oxidation, electrochemical oxidation, photochemical processes, Biological oxidation, ultrasonic treatment and Chemical oxidation such as UV-based processes as well as H_2O_2 –based processes.

CHAPTER 3

3. ADVANCED OXIDATION PROCESSES (AOP's)

Advanced Oxidation Processes AOPs were defined by Glaze 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 processes are characterized that no more toxic compound can be produced during the reaction. Also via AOP's complete organic matter minerlization could be achieved. Hydroxyl radical is specially oxidation agents that attack the majority of organic matters. The kinetic of these reactions is first order for (OH•) radical concentration, and to the species to be oxidize. Rate constant in general are in order 108-1010 M-1.s-1, where the hydroxyl radical concentration between 10-12- 10-10 M. The hydroxyl radical characterized by it is low selectivity, but it is attractive oxidants that can be used in the wastewater treatment. Several organic compounds can be eliminated or degrade immediately by use of hydroxyl radical. However, some organic are not attacked by this action like the acetic acid, oxalic acid, chlorides derivatives as chloroforms and tetrachloroethan.. The variety on AOP´s comes from the fact that there are many ways for hydroxyl radical production, this permit fulfilment for the requirements of any treatment. Above all of that, it should be taken in account that these AOP's are made by use of some expensive reactants; H_2O_2, UV and/or O_3. Thus, they should not used if there are other more economical process. Another aspect should not be forgotten in the application of the AOP's is water organic charge, in general expressed as COD (chemical oxygen demand). Normally the wastewater that has COD value below (≤10 g/L) can be treated with these processes, but if the quantity of COD is more, the necessities of the reactant are increase, with negative effect on treatment cost.

3.1 Processes based in the ultraviolet radiation

3.1.1 Photochemical process

The principle of the photochemical reaction, is the addition of energy for the chemical compound in form of radiation, which absorbed by the group of molecules to reach an excited state. The solar energy can be use as the source of such radiation energy for degradation of some compounds. But in some case this energy is not sufficient; for example, in case of phenol, solar energy is insufficient for breaking the aromatic ring. Hence, normally ultraviolet light radiation is used. Different investigation indicate that, several organic contaminants can be decomposed partial or totally into other substances less toxic and more biodegradable by oxidation based on UVlight (Oussi et al., 1997). It should be recorded that, the use of low-pressure mercury lamp, that emits light with wavelength 253.7 nm, are not efficient to eliminate all contained organic matters in water. They can be used powerfully for the degradation of the aromatics, but they are incompetent in elimination the colours aliphatic. In other hand, medium pressure mercury lamps emit spectra between 254 and 400 nm, are not only efficient in generation of hydroxyl radicals, when it is combined with H_2O_2, but also they caused electron transition in many organic matters. In the photochemical reactions, the mean step is the generation of the hydroxyl radical by photolysis of the water (Cervera et la., 1983) according to the reaction (3.2).

$$H_2O \longrightarrow H + OH\bullet \qquad (3.2)$$

This reaction is an excessive source of radicals, also in the reaction media it may generate large quantity of reaction intermediates that absorb part of the radiation, leads to considerable effect in the photooxidation kinetics of the contaminants, this make the process valid for effluents with low contaminate concentration**.** The photochemical treatment has good effect in solving the problem of refractors compound, however, it has disadvantages that it can not be applied in high scale due to ultraviolet light high production cost. Also, not all the radiation emitted by the source is used, just the absorbed radiation, and this is just small fraction of light produced attack the organic matter for chemical change, which indicate slow photodegradation kinetic. For increased the rate of This process, some additives are added like; addition of oxidant H_2O_2 and/or O_3, addition Catalyst (Photo-Fenton) or photocatalysis (TiO_2)

3.1.2 UV/H_2O_2 process

Light absorbed by a molecule can result in electronic excitation, which increases the molecule's ability to lose or gain electrons. This makes the excited state more suitable as an oxidizing or reducing agent, that in turn makes it more likely and a highly reactive species such as the hydroxide radical (OH•) can be produced from an electron transfer process between the excited state and contacting medium. The ultraviolet/H_2O_2 (UV/ H_2O_2) process involves the photolysis of hydrogen peroxide. The most accepted mechanism for this H_2O_2 photolysis is the rupture of the O-O bond by the action of ultraviolet light forming two hydroxyl radical (3.4) (Beltrán et al., 1997b):

$$H_2O_2 \longrightarrow 2OH\cdot \qquad (3.4)$$

Some of the practical difficulties with the UV photolysis of H_2O_2 are:

- Low wavelength (below 200-400 nm) is required to make the process efficient (Tachiev et al., 1998 and Helz et al., 1997).
- Turbid waters containing strong UV absorbers such as aromatics organic compounds require higher light concentration, which increases the cost of the process
- It is not applicable to in situ treatment.

The process required an acidic pH, which can be achieved sometimes by the addition of acid or ferric oxalate. The method of irradiation is not limited to the UV light and can include natural sunlight. This may require a longer processing time, but that may be outweighed by the convenience of using natural light. Chemicals that can be treated with this technique include aromatic hydrocarbons and substituted aromatic hydrocarbon, phenols, alkanes, alkynes, ethers, and ketones, both in their substituted and non substituted forms. The rate of the aqueous H_2O_2 photolysis was found to be pH dependent and increases when alkaline conditions are used, Probably because at 253.7 nm, the anions peroxide HO^{2-} has higher molar absorption coefficient (240 vs 18.6M-1.cm-1) (Glaze et al., 1987). After that the OH• radical can attack to the hydrogen peroxide leading to the following sequence of equations:

$$H_2O_2 + OH \longrightarrow HO_2\ H_2O \qquad (3.4)$$

$$H_2O_2 + HO_2 \longrightarrow OH + O_2 + HO_2 \qquad (3.5)$$

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \qquad (3.6)$$

When these reactions occur in medium that contain organic contaminate the reaction begin forming different type of radicals that degrade these contaminants. This system has advantage that if it works with ozone, it provides cheaper hydroxyl radical, which make the ozone easier to handle. The hydroxyl radical generated in presence of an organic substrate can react in three different ways (Legrini et al., 1983):

1. With hydrogen abstraction: $OH\ RH \longrightarrow R\bullet + H_2O$ (3.7)

2. with electrophilic addition: $OH\bullet + PhX \rightarrow HOPhX\bullet$ (3.8)

3. with electron transfer: $OH\bullet + RX \rightarrow RX\bullet^{+} + OH^{-}$ (3.9)

The recombination radical-radical should also be taken into account (3.10):

$$2OH^{\bullet} \longrightarrow H_2O_2 \tag{3.10}$$

Literature review show that UV/H_2O_2 has been used for degradation of different types of organic; 2, 4-dichlorophenol (DCP) and other chlorophenols removal were studied by Benítez et al. (2000a). Hirvonen et al. (2000) made a comparison between DCP degradation rate by UV/H_2O_2 process in alkaline conditions and direct UV (20-W 254 nm lamp) irradiation; in the study they reported that the addition of hydrogen peroxide at acidic pH increased the reaction rate by one order of magnitude. Alnaizy et al. (2000) studied phenol degradation with a UV/ H_2O_2 process in a completely mixed, batch photolytic reactor, the UV irradiation source was a low-pressure mercury lamp. The study indicates that there is an optimum H_2O_2/phenol molar ratio for efficient degradation in the range of 100-250.

3.1.3 Photocatalysis

The basic principle of photocatalysis process is a semiconductor photo excitation as result of radiation absorption, normally near ultraviolet 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, and react with both water and organic compounds. The holes are extremely oxidants and should thus be able to oxidize almost all chemicals, as well as water, resulting in the formation of hydroxyl radicals (Munter et al., 2001). Many catalysts have been tested, although TiO_2 in the anatase form seems to possess the most interesting features, such as high stability, good performance and low cost (Andreozzi et al., 1999). DCP complete mineralization was achieved during photocatalysis process with TiO_2 and 6-W 254 nm Hg lamp (Ku et al., 1992). Giménez et al. (1999) also tested the photocatalytic treatment of DCP by using TiO_2 and solar light, proving that reaction was first order with respect to DCP concentration and comparing the efficiencies of two different photocatalytic reactors.

3.1.4. UV/Fe (III)

UV/Fe (III) consider one of the more common treatment process based in UV-light. Fe (III) solutions in the presnce of UV irradiation acts as photo-catalyst. Throughout photo-catalytic process not only the absorbed UV photons lead to organic matter degradation but also ferric ion undergoes a photo-redox reaction producing more hydroxyl radicals.

$$Fe(III) + H_2O_2 \longrightarrow Fe(II) + OH^{\bullet\cdot} + H^+ \qquad (3.11)$$

Rodríguez et al., 2000 have been studieded the degradation of nitobenzen by UV/Fe (III) process, 80% of nitrobenzen degradation was found to achieve during 60 min irradiation time. Phenol degradation via UV/Fe (III) proceese was found to follow first orders kinetic (Rodríguez et al., 2002).

3.1.5. Fenton and Photo-Fenton

a) Fenton and Fenton like reaction

More than one century ago, H.J.H. Fenton discovered that using hydrogen peroxide and iron salt like catalyst could oxidize many organic molecules. Recently it has been discovered the mechanism of Fenton oxidation that bases on the generation of hydroxyl radical by the catalytic decomposition of the H_2O_2 in acidic media (Bigda, 1995). In presence of Fe (II), the peroxide breaks down to OH• and OH−, according to the following equations (3.14 to 3.16) (Nesheiwat and Swanson, 2000):

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + OH^- + OH^{\bullet} \qquad (3.13)$$

$$Fe(III) + H2O2 \longrightarrow Fe(II) + OH^+ + HOO^{\bullet} \qquad (3.14)$$

$$2H_2O_2 \longrightarrow H_2O + OH^{\bullet} + HOO^{\bullet} \qquad (3.15)$$

The iron catalyst can be either Fe (II) or Fe (III) salts, although ferrous iron may be preferred. Nowadays both sulfate and chloride iron salt can be used. It is interesting to note that, the possibility of iron recycling make the process more feasible, for iron recycling the procedure is the following: raising the PH, separating the iron floc, and reacidifying the iron sludge. In this process radical generation begins once the hydrogen peroxide and iron ions come in contact. The hydroxyl (OH·) radicals formed are very powerful oxidizer and are short-lived species. (OH·) is one of the most powerful oxidizer known, next to fluorine in its reactivity. The reaction rate is limited by the rate of (OH.) generation, which is directly related to the concentration of the iron catalyst, and although less so, by the specific wastewater being treated. Several mechanisms for the reaction of hydroxyl radical are possible. However, two mechanisms are most common effective in organic matter destruction. Oxygen addition mechanisms, where hydroxyl radical adds to unsaturated compound to form a free-radical product:

$$OH^{\bullet} + C_6H_6 \longrightarrow C_6H_6(OH)^{\bullet} \qquad (3.16)$$

And hydrogen abstraction, where water and an organic free radical are formed

$$OH^{\bullet} + CH_3OH \longrightarrow CH_2OH^{\bullet} + H_2O \qquad (3.17)$$

The oxidation of an aromatic ring compound such as phenol is a classic example of the use of Fenton's reagents to reduce the toxicity of industrial effluents. In the process, carboxylic and dicarboxylic acids are produced, and if the oxidation is carried to completion, CO_2 and water are formed. Substituted aromatic ring structure can be also oxidized with Fenton's reagent to carboxylic acids and dicarboxylic acids and theoretically all the way to CO_2 and water. In this way, toxic or non-biodegradable ring structure can be made less toxic and more amenable to biological oxidation. The reaction is highly exothermic and is associated with foaming and gas emissions.

b) Photo-Fenton

The degradation rate of an organic pollutant by means of Fenton or Fenton-like is strongly enhanced by UV light irradiation with wavelength superior to 200 nm (photo-Fenton and photo-Fenton like process). Under these conditions, the photolysis allows the regeneration of the Fe^{+2} by means of Fe^{+3} complexes of (3.18) (Chen et al., 1997):

$$Fe\,(OH)^{2+} \rightarrow Fe\,(II) + OH^{\bullet} \qquad (3.18)$$

Chamarro et al. (2001) used Fenton process for the degradation of phenol, 4 chlorophenol, 2, 4-dichlorophenol and nitrobenzene. The stoichiometric coefficient for Fenton reaction was approximately 0.5 mol of organic compound/mol H_2O_2. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water. Ormad et al., (2001) compared the degradation of a DCP solution by Fenton and photo-Fenton process: During Fenton reaction only a small abatement of DCP was observed, a 78% mineralizationwas achieved by the photo-Fenton process (10 mM H_2O_2, Fe (II) 10 mg.L-1, 36-W black light lamp). Recently Esplugas et al. (2002) has been studied the degradation of phenol by different oxidation processes including photo-Fenton. Fenton and photo-Fenton processes were found to be the more efficient for phenol degradation.

3.2 Ozonation (O_3)

The ozone is a powerful oxidizing agent; it is able to participate in a great number of reactions with organic and inorganic compound. Among the most common oxidizers, only hydroxyl and fluorine have oxidation potential more than the ozone. The principles disinfectant action of the ozone is known from century. However, it is in the last twenty years when this chemical agent has acquired a great importance in wastewater treatments. Thus, the ozonation can constitute an AOP's for itself, as hydroxyl radical coming from the decomposition of ozone which is catalyzed by hydroxyl ion or the initiated by the presence of traces of other substances, like transition metal cations (Beltrán et al., 1997a). Indeed, in an ozonation process, it should be considered two possible pathway of oxidation. The direct pathway through the reaction between ozone and the dissolved compounds, and radical pathway through the reaction of radicals generated from ozone decomposition (hydroxyl radical) and dissolved compounds (Baraza, 2000). The combination of both pathways for elimination of compounds depends on the nature of the compounds, the pH of the medium and of the ozone dose. On one hand, the molecular ozone can react in a direct way with the dissolved pollutants by electrophilc attack of the major electronic positions of the molecule. This mechanism predominates when the pollutant is very electophilic reagent, for example, phenols, and phenol derivatives. The reactions of the ozone with organic compound usually occurred by means of the ozonation of the double bond or in the nucliphy centre. (Non shard pair of electrons) obtaining aldehydes, acetone or carbonyls. The other mechanism, of indirect type, consists on the decomposition of the ozone to other secondary oxidants, mainly hydroxyl radical that react quickly with the pollutants. These mechanisms predominate, with low reactive molecules, such as hydrocarbons, benzene or chlorobenzene (Hoigne and Bader, 1979). Together with the process of oxidation, the ozonization diminishes the colour and the turbidity, besides disinfecting the treated waters. Another important note is that the ozone is not very selective, for what can degrade and/or eliminate the pollutants. The mechanism of the ozone decomposition in water is the following:

$$O_3 + H_2O \longrightarrow HO_3^+ + OH^- \quad (3.19)$$

$$HO_3^+ + OH- \leftrightarrow 2HO_2 \quad (3.20)$$

$$O_3 + HO_2 \longrightarrow HO + 2O_2 \quad (3.21)$$

$$HO + HO_2 \longrightarrow H_2O + O_2 \quad (3.22)$$

Numerous studies have been carried out on the reactivity of the ozone with diverse polluting substances and kinetic models of the ozonization reaction have settled down of diverse organic and inorganic compound (Hoigné and Bader, 1983 a and b). The ozone treatment process can be supplemented with the use of ultraviolet radiation and/or hydrogen peroxide.

3.2.1. UV/ O_3 process

The ozonation constitutes of the AOP's that presents several advantages in front of conventional chemical oxidizing agents, as the chlorine or the chlorine dioxide. However, refractory compound as some saturated alcohol's, coloured compound, low molecular weight compound and carboxylic acids are difficult to degrade by means of ozonation, since both ozone reactions pathway are very weak. This is due to the low value of first order kinetic constant for the direct reaction ozone-pollutant and the insufficient hydroxyl radical concentration generated by decomposition of the ozone. Unless the pH of the means rises, what would imply the use of external basic agents. Therefore a bigger concentration of radical $OH\cdot$ is needed (Beltrán et al., 1997a). The treatment with ozone can also be enhanced by use of ultraviolet radiation (254 nm) to generate more hydroxyl radicals. The extinction coefficient of the O_3 at 254 nm is of 3300 $M^{-1}.cm^{-1}$, which is very superior that of the H_2O_2 (Andreozzi, 1999). If an effluent, which has dissolved ozone, is exposed to the UV radiation, photolysis takes place, by dissociation of O_2 molecule to oxygen atom in the state $_1D$. This the last one can react with a molecule of water to produce hydrogen peroxide that in turn can be decomposed by photolysis or to react with the ozone. The global reaction that takes place is the following:

$$H_2O + O_3 \longrightarrow 2OH^{\bullet} + O_2 \qquad (3.23)$$

3.2.2 H_2O_2 / O_3 process

Another way to increase the production of hydroxyl radical is combination of ozone with hydrogen peroxide. This combined system produces bigger conversion yields than the ozonation. It can be used in those cases that the direct reaction ozone-pollutant follows a slow kinetic regime. Hydrogen peroxide in water break-up and partially dissociated in the species of ionic (HO_{2}-), which reacts with ozone causing the decomposition of the last giving a series of reactions. By that both radical's hydrogen peroxide and ozone participate in the reaction and degrade more effectively the existence organic (Adam et al., 1994). The global reaction that takes place is (3-26):

$$H_2O_2 + 2O_3 \longrightarrow 2OH^{\bullet} + 3O_2 \qquad (3.26)$$

That has as initiation stage (3.27) (Staehelin and Hoigne, 1982):

$$HO^{-}_{2} + O_3 \longrightarrow OH_2^{\bullet} + O_3^{\bullet} \qquad (3.27)$$

Because this system doesn't depend on the radiation transmission to activate the molecules of O_3 or H_2O_2, its biggest advantage is being able to work without problems in cloudy waters. The process H_2O_2/O_3 has been studied with several compounds, it gives bigger degradation rate. With several compounds it has been a gaussiana relationship, increased the degradation speed with the quantity of peroxide, until a point for which the reaction is inhibited, because the excess H2O2 consume radical hydroxyl in the reaction (3.28) (Chamarro et al, 1996):

$$H_2O_2 + OH^{\bullet} \longrightarrow HO^{\bullet}_{2} + H_2O \qquad (3.28)$$

Paillard et al., (1988) studied the degradation of herbicides (s-triazina) found that the good relationship (mg of hydrogen peroxide/mg ozone) was around 0, 5. Studies regarding DCP removal by the O_3/UV process (e.g. Trapido et al., 1997; Hautanemi et al., 1998; Kuo, 1999) have been studied the degradation of DCP by different ozone combination.

3.2.3. UV/H_2O_2 / O_3 process

Another possible alternative for the obtaining more hydroxyl radical is to combine the binary systems UV/ H_2O_2, O_3/UV and O_3/ H_2O_2, obtaining the tertiary system O_3/UV/ H_2O_2. This process is very potent and it allows a considerable reduction of the total carbon and/or quick mineralization of pollutants. It is the most effective treatment for highly polluted effluents. In accordance with the stiochiometry. Two ozone molecules eliminated by molecule of peroxide produce two hydroxyl radical according to:

$$2O_3 + H_2O_2 \longrightarrow 2OH^{\bullet} + 3O_2 \qquad (3.29)$$

Zeff and Barich (1990) studied the oxidation of different organic compound in water, as Methlyne chloride, chlorobenzene, benzene, toluene, ethilbenzen, trichloroethilen, etc by means of this system, and they proved that this method is more efficient than the treatment ofeach treatment alone or in binary combinations. Mokrini et al., (1997) studied the effect of this combination in the phenol oxidation at different pH. A 40% of TOC reduction was achieved by this method. With regard to DCP, no articles have been found in the literature about the oxidation of these compounds by means of this process.

3.2.4. O_3/UV/Fe process

The combination of ozone with light and iron as catalyst improves the oxidative capability of the catalytic ozonation O_3/Fe. Three processes may account for this improvement of the efficiency of the process. On one hand, Fe(III) species undergo a photoredox process with UV and near-UV light, giving rise to Fe(II) and $OH^{\cdot}$ radicals according to equation 3-34 (Safarzadeh-Amiri et al., 1996; Mazellier et al., 1997):

$$Fe^{3+} \longrightarrow Fe^{2+} + OH^{\bullet} + H^{+}$$

On the other hand, Fe(III) is considered to increase the number of hydroxyl radicals through the reduction of O_3 with the Fe_{2+} generated by the photoreduction of Fe_{3+} (Abe and Tanaka, 1999), similar to the mechanism proposed for the photo-Fenton reaction. The mechanism is quite unclear (Ruppert et al., 1994)

$$Fe2+ + O_3 \longrightarrow FeO^{2+} + O_2 \qquad (3.31)$$

$$FeO^{2+} + H_2O \longrightarrow Fe^{3+} OH + OH^{-} \qquad (3.32)$$

If hydrogen peroxide is present in the medium, directly or by ozone photolysis, it can react with Fe(II) by Fenton reaction (3335), regenerating Fe(III) and closing a loop mechanism Fe(III)/Fe(II) while hydroxyl radicals are generated.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (3.33)$$

Besides this, the initial oxidation of organic pollutants generates oxygenated intermediates, e.g. intermediates with carboxylic functional groups, which can react with Fe (III) and form complexes. These complexes are also photoactive and produce CO2, organic radicals and ferrous ions on irradiation, contributing to the mineralization of these pollutants without the participation of hydroxyl radicals (Safarzadeh-Amiri et al., 1996a; Abe and Tanaka, 1999).

$$RCO_2 + Fe(III) \longrightarrow R^\bullet + CO_2 + Fe(II) \qquad (3.34)$$

The addition of iron ion (Fe^{3+} or Fe^{2+}) has been reported to accelerate the UV-enhanced ozonation of several pollutants (Abe and Tanaka, 1997, 1999). Ruppert et al. (1994) studied the degradation of 4-chlorophenol solutions by means of different AOPs. The O_3/UV/Fe (II) was found to be the most effective method, achieving complete mineralization in few minutes. Complete mineralization of DCP among other chlorophenols was achieved also by O_3/UV/Fe (III) as reported by Abe and Tanaka (1997), where the effect of Fe (III) was found to depend on its concentration. Abe and Tanaka as well (1999) studied the effect of this combination with nitrophenols, attributing the main effect to the photodegradation of aliphatic intermediates by Fe (III) complex. The degradation of aniline and 4-chlorophenol has been studied by Sauleda and Brillas (2001) by means of O_3/UVA/Fe (II), reporting that both quickly mineralized by the O_3/UVA and O_3/UVA/Fe (II).

3.3 Photolysis

The word photo catalysis is composed of two parts:

1. The prefix photo, defined as "light".
2. Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

Hence, photo catalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved it self

3.3.1 Principles

Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (ca. 3.2 eV for anatase), producing electron-hole (*e-*/*h+*) pairs, as written in the equation (1)

$$TiO_2 \quad \rightarrow \quad ecb\,(TiO_2) + h+\,vb\,(TiO_2) \qquad [1]$$

Where cb is conduction band and vb is the valence band.

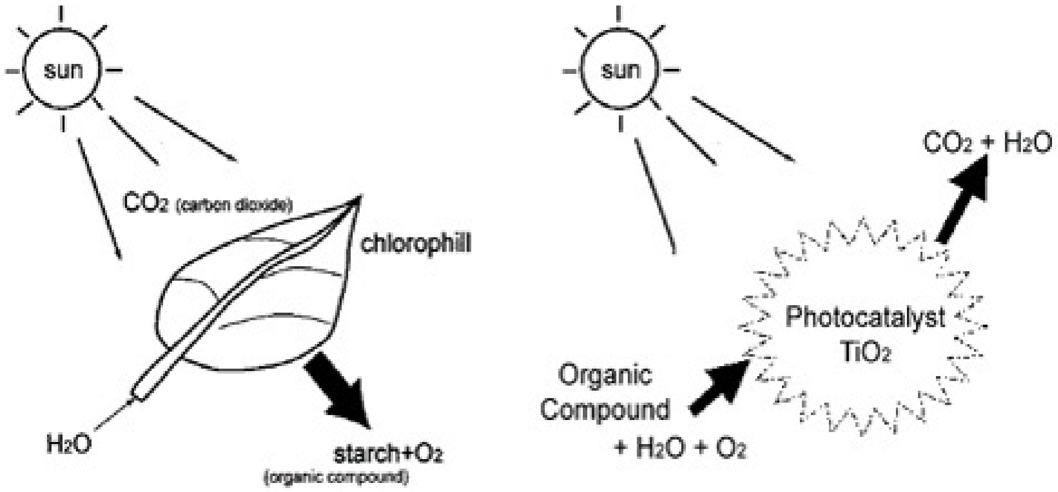

Fig-3.1The Photocatalytic reaction in plant is basically similar to the Photocatalytic reaction in TiO_2

Consequently, following irradiation, the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding medium. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical effect. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the external surface, the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion (OH^-), organic compounds, or oxygen. The charges can react directly with adsorbed pollutants, but reactions with water are far more likely since the water molecules are far more populous than contaminant molecules. Oxidation of water or OH^- by the hole produces the hydroxyl radical (•OH), an extremely powerful and indiscriminant oxidant. For a comparison, the oxidation potential of hydroxyl radical (•OH) is 2.8 V relative to the normal hydrogen electrode (NHE); cf. other substances used for water disinfection: ozone (2.07 V), H_2O_2 (1.78 V), HOCl (1.49 V) and chlorine (1.36 V). OH radicals rapidly attack pollutants at the surface, and possibly in solution as well, and are usually the most important radicals formed in TiO_2 photocatalysis. An important reaction of the conduction band electron is reduction of adsorbed O_2 to O_2•□. This both prevents the electron from recombining with the hole and results in an accumulation of oxygen radical species that can also participate in attackingcontaminants

3.3.2 Mechanism of generation of oxidation species

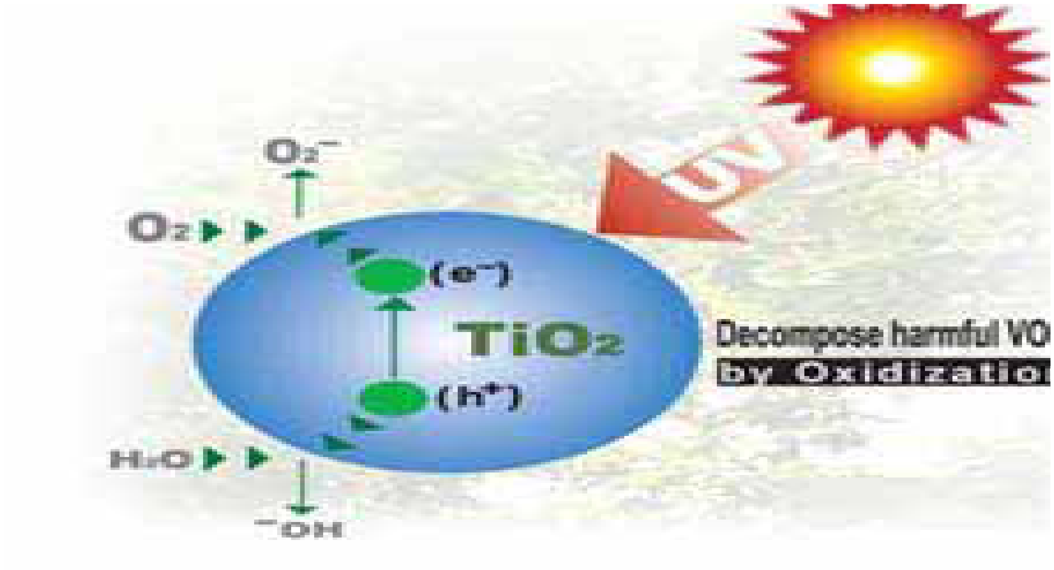

Fig-3.2 Mechanism of generation of oxidation species

Heterogeneous photocatalysis is a complex sequence of reactions. Pirkanniemi suggested in 2002 that the heterogeneous photocatalysis reaction follows five steps. These are:(i) diffusion of reactants to the surface, (ii) adsorption of reactants onto the surface, (iii) reaction on the surface, (iv) desorption of products from the surface, and (v) diffusion of products from the surface" There are two routes through which OH radicals can be formed. The reaction of the valence-band "holes" (hvb+) with either adsorbed H_2O or with the surface OH^- groups on the TiO_2 particle.[1] equations (1-2 and 1-3).

$$TiO_2\ (hvb+) + H_2Oads \rightarrow TiO_2 + HO\bullet\ ads + H+ \qquad [2]$$

$$TiO_2\ (hvb+) + HO^-ads \rightarrow TiO_2 + HO\bullet ads \qquad [3]$$

In general, donor (D) molecules such as H_2O will adsorb and react with a hole in the valence-band and an acceptor (A) such as dioxygen will also be adsorbed and react with the electron in the conduction band (ecb), according to equations 1-4 and 1-5

$$\mathrm{TiO_2\,(hvb+)\ +Dads \rightarrow TiO_2 + D+ads} \qquad [4]$$

$$\mathrm{TiO_2\,(ecb-)\ +Aads \rightarrow TiO_2 + A-ads} \qquad [5]$$

It is generally accepted that oxygen plays an important role. Oxygen can trap conduction band electrons to form superoxide ion (O_2 • □), equation (6). These superoxide ions can react with hydrogen ions (formed by splitting water), forming HO2•

$$\mathrm{TiO_2(ecb-) + O_2ads + H+ \rightarrow TiO_2 + HO_2{\bullet} \rightarrow O_2 \bullet} \,\square\, \mathrm{+ H+} \qquad [6]$$

H_2O_2 could be formed from HO_2 • via reactions (1-7)

$$\mathrm{TiO_2(ecb-) + HO_2{\bullet} + H+ \rightarrow H_2O_2} \qquad [7]$$

Cleavage of H_2O_2 by one of the reactions (8, 9, and 10) may yield an OH radical

$$\mathrm{H_2O_2} + hv \rightarrow \mathrm{2HO{\bullet}} \qquad [8]$$

$$\mathrm{H_2O_2 + O_2{\bullet} \rightarrow HO{\bullet} + OH{\bullet}} \qquad [9]$$

$$\mathrm{H_2O_2 + TiO_2(ecb-) \rightarrow HO{\bullet} + HO- + TiO_2} \qquad [10]$$

Photoreduction, photooxidation and adsorption occur on or near the particle surface. A competition reaction occurs between water, oxygen, organic molecules and trace metals which may be present in the System.

3.3.3 TiO_2 as a photocatalyst

It is known that photo catalysts can be either homogeneous or heterogeneous. In a system where a homogeneous photo catalyst is used, the photo catalytic reaction takes place in a homogeneous liquid phase. Examples of such photo catalysts include dye, soluble metal catalysts like copper complexes, tin chloride, palladium chloride, Fenton reagent and hydrogen peroxide.

On the other hand, if a heterogeneous photo catalyst is used the photo catalyst and reactant are present in different phases and the photo catalytic reaction occurs at their interface. Examples of heterogeneous photo catalysts include poiyoxometallates such as $Cs_3PW_{12}0_{40}$, TiO_2, in the colloidal and powdered form or dyes supported on glass, sand and other materials. Solid TiO_2 absorbs light in the near UV (-350 nm) causing an electron from the valence band to be excited across the band gap of +3.0 eV up to the conduction band containing free electrons.

3.4 Application of advanced oxidation processes (AOPs)

Since 1972, when Fujishima and Honda discovered the photocatalytic splitting of water using TiO_2 electrodes; research on the heterogeneous photocatalysis started growing rapidly. The research work focused on energy storage, and in recent years applications have been directed towards environmental clean-up. Applications of this technique have been implemented in many fields such as, drinking water treatment, industrial, and health applications.

3.4.1 Removing trace metals

Trace metal such as mercury (Hg), chromium (Cr), lead (Pb) and others metals are considered to be highly health hazardous. Thus, removing these toxic metals are essentially important for human health and water quality. The environmental applications of heterogeneous photocatalysis include removing heavy metals such as (Hg), chromium (Cr), lead (Pb), Cadmium (Cd), lead (Pb), Arsenic (As), nickel (Ni) cupper (Cu).

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3.4.3 Removing inorganic compounds

Inorganic species such as bromate, or chlorate, azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed. Metal salts such as $AgNO_3$, HgCl and organometalic compound (e.g CH_3HgCl) can be removed from water, as well as cyanide, thiocyanate, ammonia, nitrates and nitrites by photocatalytic treatment.

Fig-3.3 Properties of Photocatalyst

3.4.4 Water Purification

Photocatalyst coupled with UV lights can oxidize organic pollutants into nontoxic materials, such as CO_2 and water and can disinfect certain bacteria. This technology is very effective at removing further hazardous organic compounds (TOCs) and at killing a variety of bacteria and some viruses in the secondary wastewater treatment. Pilot projects demonstrated that photocatalytic detoxification systems could effectively kill fecal coli form bacteria in secondary wastewater treatment.

3.5 Light sources

TiO_2 absorbs radiation below the visible range of light spectrum. Hence, photoactivation of TiO_2 requires radiation with light of wavelength less than or equal to 384 nm, with an absorbance maximum at approximately 340 nm. The vast majority of studies quoted in the literature have been carried out between the wavelengths 320- 380 nm. The light that gives rise to the required radiation field can be produced by artificial lamps or by solar irradiation. In a photocatalytic reactor, UV-A (320-380 nm) radiation is provided by fluorescent low-pressure mercury lamps emitting low-intensity UV-A radiation. Medium pressure mercury lamps have also been used, which emit high intensity UV light in the short, medium and long UV spectrums. However, short (UV-C; 200-280 nm) and medium (UV-B; 280-320 nm) UV radiation emitted by the mercury is usually cut off by the photoreactor material, unless it is made of quartz. Some studies have also reported increased efficiency with UV-C radiation than UV-A for the degradation of certain organic materials. Direct photolysis and the higher probability of trapping of electron-hole pairs with shorter wavelength excitation were thought to be the possible reasons for such an effect. It is estimated that only 5% of the incident solar irradiation is of use for the TiO_2 band gap photocatalytic reaction. This significantly limits its practical application. Therefore, modification of TiO_2 photocatalysts to enhance light absorption and photocatalytic activity under visible light irradiation is the subject of recent research

CHAPTER 4

4. LITERATURE REVIEW

The presence of highly biorecalcitrant organic contaminants in the environment due to industrial and intensive agricultural activities is of particular concern for the preservation of aquatic ecosystems. Advanced oxidation processes (AOP) have shown to rapidly degrade many different biorecalcitrant compounds. A good solution to this drawback is to reduce the use of AOP to strictly produce a non-toxic and biodegradable intermediate solution that could be treated in a biological secondary step. Complete mineralization of the contaminants may be achieved with a partial use of AOP and a complementary biological treatment. Advanced Oxidation Processes (AOPs) use as a pre-treatment step for the enhancement of the biodegradability of wastewater containing recalcitrant compounds can be justified if microorganisms in a biological treatment readily degrade the intermediates resulting from the reaction. Therefore, the coupling of AOPs and biodegradation has a great advantage over either treatment alone in the remediation of organic contaminants.

4.1 Photocatalytic degradation of synthetic dye

Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution was studied by M.A. Rauf et.al. (2009). This review will attempt to summarize and highlight the effect of a variety of conditions on TiO_2-photocatalysed decoloration of dyes, such as amount of catalyst, reaction pH, light intensity, concentration of organic dye, and the presence of additives such as ions. This review also summarizes the degradation pathways that azo dyes undergo, with some of the intermediates that are generated during their degradation. Finally, a survey is presented of the various classes of dyes and their relative ease of degradation by AOPs.

Literature survey it has been found that operating pH of solution significantly affects catalyst activity. Montaser Y. Ghalya et al. (2006) has been investigated the effect of pH in the range 2-10 for the degradation of simulated degradation of Maxoline Navy 2 RM basic dye in aqueous solution with TiO_2-A (pure anatase) as photocatalyst in slurry form. It is observed that elevating the pH of simulated, significantly improved the COD removal efficiency.

Blanca E. Barraga et al. (2006) reported the Biodegradation of azo dyes by bacteria inoculated on solid media. Bacteria were inoculated on different solid media to attain biodegradability of an azo dye (Acid Orange 7). Kaolin, bentonite and powdered activated carbon (PAC) were selected to be used with cultures of Enterobacter, Pseudomonas and Morganella sp., as bacteria would be able to degrade several textile dyes. For the solid, to be employed as media, special characteristics are needed with regards to adsorption capacity for concentrating substrate within the cell environment and an adequate particle size and surface texture for assuring bacterial colonization. Only PAC with 0.490 mm particle size shows these characteristics among the solids used and it was colonized by a high number of cells from the three cultures. Dye was degraded following asecond-order kinetics. A mechanism for dye degradation is proposed in which anaerobic and aerobic microniches in the PAC particle perform cleavage of the azo bond and oxidation of the amines formed in the same biocatalytic particle.

Brijesh Pare et al (2008) worked on the ZnO assisted photocatalytic degradation of acridine orange in aqueous solution using visible irradiation. Photocatalytic degradation of the dye, acridine orange, has been carried out in aqueous heterogeneous medium containing ZnO as photocatalyst in a batch reactor. Visible light in the absence of ZnO has negligible effect on degradation. The total degradation of dye was tested using the chemical oxygen demand (COD) method. The addition of an optimal amount of hydrogen peroxide and potassium persulphate increases the degradation rate while NaCl and Na_2CO_3 decrease. Bubbling of nitrogen in the reaction solution decreases the reaction rate. ZnO has been found experimentally to be a highly efficient photocatalyst for the degradation of acridine orange dye and hence there is a great potential in the treatment of organic pollutants such as dyes.

S. Anandan et al investigated the effect of loaded silver nanoparticles on TiO_2 for photocatalytic degradation of Acid Red 88. Nanometer sized Ag–TiO_2 nanoparticles were prepared (by photoreduction of Ag^+ ions) in order to assess its photocatalytic degradation ability of target pollutant (textile dye; Acid red 88) upon visible light irradiation. Mineralization of target pollutant was also performed by total organic carbon (TOC) analysis and from the results, it was confirmed that 65% mineralization was achieved in 7 h using PMS as electron acceptor. Overall, this system is relatively inexpensive, reproducible, extremely stable and efficient in complete degradation of dye in aqueous solution. In order to obtain maximum information about the performance of Ag–TiO_2 photocatalyst, we did experiments under different operating conditions, i.e., variation of amount of catalyst, concentration of dye and electron acceptors. In addition to the above, a comparative study on the photocatalytic activities of TiO_2 was also made.

Panneer Selvam Sathish Kumar et al studied on the Photocatalytic degradation of Acid Red 88 using Au–TiO_2 nanoparticles in aqueous solutions. Metal loaded semiconductors in general possess greater photocatalytic activity than pure semiconductors. Hence, with an attempt to achieve higher photocatalytic activity, Au–TiO_2 photocatalysts were prepared by deposition–precipitation method. A possible mechanism for the photocatalytic degradation of AR88 by Au–TiO_2 in the absence and presence of other oxidizing agents (peroxomonosulfate (PMS), peroxodisulfate (PDS) & hydrogen peroxide (H_2O_2)) has been proposed. The extent of mineralization of the target pollutant was also evaluated using Total Organic Carbon (TOC) analysi

Hu Chun and Wang Yizhong have been studied the photodegradation and biodegradability for four non-biodegradable commercial azo dyes, Reactive YellowKD-3G, Reactive Red 15, Reactive Red 24, Cationic Blue X-GRL, an indicator. The color removal of dyes solution and dyeing wastewater reached to above 90% within 20–30min. of photocatalytic treatment. Biochemical oxygen demand (BOD) was found to increase, while chemical oxygen demand (COD), total organic carbon (TOC) decreased, so that the ratio of BOD_5/COD of the wastewater increased from original zero up to 0.75. The result indicate that photocatalytic oxidation enhanced the biodegradability of the dye-containing wastewater. When the color disappeared completely, the wastewater biodegraded normally and could be discharged for further treatment. The experimental results demonstrate that it is possible to combine photocatalysis with biological treatment for the remedy of wastewater containing generally non-biodegradable azo dyes.

4.2 Photocatalytic degradation of commercial dye

A bench-scale study combining photo-Fenton reaction with an aerobic sequencing batch reactor (SBR) to degrade a commercial homo-bireactive dye (Procion Red H-E7B, 250 mg l^{-1}) was investigated by Julia García-Montaño and José A. García-Hortal (2005). The photo-Fenton process was applied as a pre-treatment, avoiding complete mineralisation, just to obtain bio-compatible water able to be treated by means of the SBR in a second step. In this sense, different Fenton reagent concentrations were assessed by following dye solution biodegradability enhancement (BOD_5/COD), as well as the DOC, colour ($Abs_{543.5}$) and H_2O_2 evolution with photo-Fenton irradiation time. Obtained pre-treated solutions were biologically oxidized in a SBR containing non-acclimated activated sludge. Different hydraulic retention times (HRT) in the bioreactor were tested to attain the maximum organic load removal efficiency.

Ozonation of aqueous solution of Procion red MX-5B, a commercial azo reactive dye have been reported by K. Pachhade & K. Swaminathan (2008). The effect of various experimental variables on decolorization and degradation of the dye has been studied. Color removal was faster than organic removal. Dye mineralization was evident by the generation of sulphate, chloride, nitrate, oxalic and acetic acid during ozonation. Among the metal ions studied, manganese catalyzed ozonation showed better decolorization. Acetyl benzoic acid, diethyl phthalate and phthalic anhydride were identified as intermediates by gas chromatography mass spectra (GC/MS). Based on these findings a tentative pathway for the degradation MX-5B was postulated

The photooxidation Procion Yellow H-4R dyes, Bright Blue Remazol (blue reagent-19), Red Procion H-E7B, and the mixture of the two last dyes were investigated by Francisco A. P. Costa and Jorge Nozaki (2004). The efficiency of photooxidation were compared using hydrogen peroxide as a bleaching reagent, solar and ultraviolet radiation. The completely degradation of blue dye and a mixture of blue and red dyes were almost after 3 h, either by solar or ultraviolet radiation.

Francesc Torrades et.al. (2004) reported the degradation of different commercial reactive dyes: a monoreactive dye (Procion Red H-E7B), and hetero-directive dye (Red Cibacron FN-R) and a Standard Trichromatic System, by using solar light assisted Fenton and photo-Fenton reaction. The reaction efficiencies have been compared with the ones obtained for the same system in the dark or under the assistance of an artificial light source. The use of solar light is clearly beneficial for the removal of color, aromatic compounds (UV_{254}), total organic carbon (TOC), and the increase of the BOD_5/COD ratio. The possibility of a combined advanced oxidation process (AOP)/biological treatment based on the use of sunlight is suggested.

M.A. Barakat et.al(2010) studied on the adsorption and photodegradation of Procion yellow H-EXL dye over TiO_2 suspension has been investigated. The photocatalytic process used the photogenerated holes and hydroxyl radicals as oxidizing species for the dye. Different parameters affecting the adsorption and photocatalytic degradation processes such as solution pH, initial dye concentration, and TiO_2 dosages were investigated. The dye removal % is inversely proportional to its concentration, the lower the dyes concentration, the higher the efficiency of dye removal. The efficiency values of both adsorption and photocatalytic degradation processes reached maximum value .

Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of H_2O_2/UV, Fenton, UV/Fenton, TiO_2/UV and TiO_2/UV/H_2O_2 processes were investigated by A. Riga & V. Karayannis (2006). The decolorization (determined by spectrophotometric analysis) and the degradation were compared for the different processes examined. The decolorization of the Procion H-exl solutions considered was found to strongly depend on the system parameters in all five AOPs. Although decolorization is very fast for the Fenton process and becomes even faster for the UV/Fenton process, degradation rates are relatively low for these two methods. Addition of H_2O_2 increases the decolorization and especially the degradation rates for the TiO_2/UV process. The H_2O_2/UV and TiO_2/UV/H_2O_2 processes result in the fastest dye degradation. The addition of the salts examined has in general an adverse effect on the decolorization rates, but to a varying degree depending on the salt used.

Degradation of eight commercial reactive azo dyes with different structures containing different substituted groups a semi-batch reactor by ozonation individually and in mixture has been investigated by K. Sarayu et al (2005). The results showed that pH 10 was effective for color and COD removal of these dyes. Maximum colors and

COD removal could be achieved at an ozone dose of 4.33 mg l_1 at 30 min. Oxidation and cleavage of substituent groups were evidenced by the release of chloride, nitrate and sulfate during ozonation. Increase in biodegradability was observed after ozonation, as measured by the BOD_5/COD ratio. The ozonation reaction followed a pseudo first order kinetics. The results of the present study have clearly demonstrated that ozonation proes to be a viable technique for the treatment of highly recalcitrant azo dyes containing wastewater

F. Harrelka et al studied on the Photocatalytic and combined anaerobic–photocatalytic treatment of textile dyes. A photocatalytic process based on immobilized titanium dioxide was used to treat crude solutions of azo, anthraquinone and phthalocyanine textile dyes. Photocatalysis was able to remove more than 90% color from crude as well as autoxidized chemically reduced dye solutions. UV-absorbance and COD were also removed but to a lower extent (50% in average). The end products of photocatalytic treatment were not toxic toward methanogenic bacteria. The results demonstrate that photocatalysis can be used as a pre- or post-treatment method to biological anaerobic treatment of dye-containing textile waste.

Pandurangan et al., (2001) carried out the photocatalytic degradation of textile dye, Basic Yellow Auramine O by a batch process using ZnO as the catalyst and sunlight as the illuminant. In addition to removing the color from the dye solution, the COD was also reduced suggesting that the fragments produced from the dye were mineralized. The photocatalytic degradation of Crystal Violet, a triphenyl methane dye (also known as Basic Violet 3) in aqueous solutions was investigated with Ag+ ion doped TiO_2 under UV and simulated solar light by Sahoo et al., (2005). The dye (20 ppm) was found to degrade about 88% after illumination for 10 h.

4.3 Photocatalytic degradation of textile wastewater dye

A. Alinsafi et. al.,2007 have applied photo catalysis with TiO_2 particles immobilised either on a glass slide or on a non-woven glass fiber fabric has been applied to pure reactive dyes' (azoïc and metal phthalocyanines) solutions as well as textile wastewater containing the same dyes under UV and solar irradiation. Decolourization of textile wastewater was in the range 21–74% under solar irradiation, with COD removal rate between 0.2 and 0.9 g COD/h/m_2. Performance prediction is therefore difficult but the results are encouraging for textile wastewater remediation. No pH adjustment is necessary and wastewater at high pH can be treated directly after suspended solids removal.

Different parameters were investigated to evaluate their effect on the process removal efficiency of reactive dye from simulated spent reactive dye bath, by solar / TiO_2 / H_2O_2, including H_2O_2 concentration, TiO_2 loading and pH. As a result 99% of reactive dye can be removed at a TiO_2 loading of 400mg/l, H_2O_2 concentration of 150 mg/l and of pH: 5.2. The effect of photocatalytic deactivation of TiO_2 on reactive dye removal was studied for ten number of cycles, and found that the extent of deactivation was high for each consecutive repeated use (*S. S.Reddy et.al, 2005*)

Pekakis PA et.al., 2006 investigated the oxidative degradation of an actual textile dye house wastewater by means of photo catalysis. The UV-A-induced Photocatalytic oxidation over TiO_2 suspensions was capable of decolorizing the effluent completely, as well as reducing chemical oxygen demand (COD) sufficiently (COD reduction generally varied between about 40% and 90% depending on the operating conditions) after 4 h of treatment. Two crystalline forms of TiO_2, viz. anatase and rutile, were tested for their photocatalytic activity and anatase was found to be more active than rutile. To assess catalyst activity on repeated use, experiments were performed where the catalyst was recovered and reused. Finally, the luminescent marine bacteria Vibrio fischeri was used to assess the acute ecotoxicity of samples prior to and after the photocatalytic treatment.

Joshi P et. al., 2001 studied the photocatalytic degradation of two simulated textile dye bath wastewaters. Dye bath wastewaters were subjected to photodegradation in a batch annular immersion well photo reactor equipped with a 400W Medium Pressure Mercury Lamp (MPML). The UV illuminated TiO_2 containing aqueous suspensions found to remove color as well as chemical oxygen demand (COD). The photocatalytic activity was monitored by measuring the rates of decolorization and CODremoval as a function of concentration of the dye and treatment time. The first order rate constant (k (app)) for decolorization was 3-9 times higher than the k (app) for COD removal.

Heterogeneous photocatalytic oxidation of contaminants present in wastewater produced by a textile industry was carried out. The samples were withdrawn from the plant before and after a traditional biological treatment. The effluents were named A and

A' (before the biological treatment), B and B' (after the biological treatment). Polycrystalline TiO_2 (Degussa P25) was used as the catalyst in a batch photoreactor with immersed lamp. An almost complete decolorization was observed after about 0.5 divided by 1 hour for both kinds of effluents, but the decrease of the total organic carbon (TOC) concentration occurred more slowly. The influence of some chemical oxidants, i.e. ozone, hydrogen peroxide and peroxydisulfate on the photo-oxidation rate was also investigated. After addition of H_2O_2 or S_2O_8 (2-) TOC decreased more quickly only for B and B'. The runs performed by using O_3 as bubbling gas showed a mineralization rate higher than that observed in the presence of O_2 (*Augugliaro V et. al., 2002*).

Hu. C et. al., 1999 have been investigated the photodegradation one industrial wool textile wastewater, using TiO_2 suspensions irradiated with a medium pressure mercury lamp. The color removal dyeing wastewater reached to above 90% within 20- 30 min. of photocatalytic treatment. Biochemical oxygen demand (BOD) was found to increase, while chemical oxygen demand (COD), total organic carbon (TOC) decreased, so that the ratio of BOD_5/COD of the wastewater increased from original zero up to 0.75. The result implies that photo catalytic oxidation enhanced the biodegradability of the dye-containing wastewater and therefore relationship between decolorization and biodegradability exists.

Heterogeneous photocatalysis may be considered a viable alternative for the removal of refractory organics due to several important advantages such as: complete mineralization or formation of more readily biodegradable intermediates when complex organic compounds are treated, no need of auxiliary chemicals, no residual formation, easily operation and maintenance of the equipment. This paper presents a literature survey of the research conducted in the field of heterogeneous photocatalysis, providing information on the possibilities and efficiencies encountered in the application of this process for industrial wastewater treatment for the removal of different types of refractory organic compounds (*Anca F. C. et. al., 2002*).

Photo degradation of a real textile dyeing wastewater taken from Hilla textile factory in Babylon Governorate, Iraq has been investigated. Photocatalytic degradation was carried out over suspensions of titanium dioxide or zinc oxide under ultraviolet irradiation. Photodegradation percentage was followed spectrophometrically by the measurements of absorbance at max equal to 380 nm. The rate of photo degradation increased linearly with time of irradiation when titanium dioxide or zinc oxide was used. A maximum color removal of 96% was achieved after irradiation time of 2.5 hours when titanium dioxide used at 303K and 82% color reduction was observed when zinc oxide used for the same period and at the same temperature. The effect of temperature on the efficiency of photo degradation of dyestuff was also studied. The activation energy of photo degradation was calculated and found to be equal to 21 ± 1 kJ mol-1 on titanium dioxide and 24 ± 1 kJ mol-1 on zinc oxide (*Abbas J. A. et. al., 2008*).

Several systems are used in photocatalytic degradation; two of them are experimented in the treatment of textile dyes and washing out reagents. The Thin Fixed Film Bed Reactor (TFFBR) and Aerated Cascade photocatalytic reactor ACP models developed to investigate photocatalytic degradation of organic compounds. For the firstone the catalyst is fixed while, for the second one the catalyst is hanging in the solutions. The efficiency of the two systems is tested for the solar catalytic treatment of commercial dyes and washing out reagents. The degradation of the black, red, blue and golden dyes shows that the black had the highest TOC degradation than others. Moreover the ACP system was more efficient than TFFBR. The treatment of the washing out reagents in suspended solutions and TFFBR reactor gives a high TOC degradation with the last system comparing to the first one (*Ghozzi K. et.al.,2002*).

M. Muthukumar et al. (2003) reported Optimization of ozone treatment for color and COD removal of acid dye effluent using central composite design experiment. Acid Red 88 dye is used for this study and the salt additive sodium sulphate is varied between 5 and 15 g/l, pH is between 3 and 11 and the treatment time is varied between 30 and 360 s. It is observed from the results that the treatment time plays a major role in decolouration and COD removal of the dye effluent. The increasing decolouration efficiency is obtained with increasing treatment time. At neutral pH, the efficiency of ozone is low in terms of decolouration when compared with that at acidic and alkaline pH. Lower salt concentration gives faster decolouration of the effluent while increasing the salt concentration interferes with the decolouration efficiency. Maximum COD removal of 64% is obtained at lower salt concentration in about 195 s at alkaline pH.

F. Al-Momani et.al (2002) have been studied photo-degradation and biodegradability for three different families of non-biodegradable textile dyes (Intracron reactive dyes, Direct dyes and Nylanthrene acid dyes) and a textile wastewater, using VUV photolysis. 90% of color removal of dye solutions and wastewater is achieved within 7 min of irradiation. Biological oxygen demand (BOD) was found to increase during discoloration process while chemical oxygen demand (COD) decreased. The biodegradability index (BOD_5/COD) increases up to 0.40 for most of the dye solutions when total discoloration is obtained. It implies that VUV photolysis tends to enhance the biodegradability of dye containing solutions.

Ma Cristina Yeber et.al (2000) reported the use of photocatalysis to degrade two bleaching effluents from *P. radiata* (D_oE_{op}) and *E. grandis* (CEop) wood processing. Organic matter oxidation was followed by general parameters (TOC, color, AOX), toxicity and biodegradability. Reactions with suspended and supported catalysts, TiO_2 and ZnO, were carried out for comparison. For both effluents, photocatalytic treatment led to an improvement in biodegradability and a reduction in acute toxicity.

The degradation of two polluted textile wastewaters from SOITEX (silk and textile) industry using the plasma-catalytic process, by non-thermal Gliding arc technique coupled to Degussa P25 titanium dioxide (TiO_2) as photo-catalyst has been studied by M.R. Ghezzar et.al (2007). The results showed that maximum degradation was attained for $3\ g\ L^{-1}$ TiO_2 concentration. For wastewater (1) degradation was 95% at the end of 60 min of treatment time. The same wastewater was completely decolourised after only 30 min of plasma-catalytic treatment time. In parallel, the biodegradability was significantly enhanced through 20 min of exposure to the plasmagenous source for both wastewater samples. Turbidity of wastewater (1) and wastewater (2) decreased with rate constants of 0.015 and $0.017\ min^{-1}$, respectively. The TiO_2-mediated Gliding Arc discharge (GAD_{TiO2}) showed potential application for the treatment of liquid wastes, resulting in the mineralization of the wastewater samples confirmed by chloride, sulphate and phosphate ions formation. In both cases of GAD treatments, with and without photo-catalyst, the plasmagenous process proves efficient in the field of wastewaters degradation.

V. Sarria, et al (2006) studied on the mineralization of 5-amino-6-methyl-2-benzimidazolone (AMBI), an important precursor in the industrial production of dyes, through an integrated Fe(III) photoassisted– biological system without addition of other electron acceptor than O_2. The iron photoassisted process produces a biocompatible solution, removing 100% of the initial biorecalcitrant compound and 40% of the Dissolved Organic Carbon (DOC), and then the complete mineralization was achieved in the biological treatment. The following steps are involve in this study :(a) the UV-Vis spectroscopic characterization of Fe(III), AMBI, and its mixture in aqueous solution, (b) the involvement of √OH radicals and oxygen in the photodegradation of AMBI, (c) the comparison between O_2 and H_2O_2 as electron acceptors in the iron photoassisted pretreatment. The obtained results indicate that a coupled solar– biological treatment system at pilot scale is a possible way to achieve the complete mineralization of biorecalcitrant pollutants.

Treatment of textile industry wastewater by supported photocatalysis was investigated by A. Alinsafi and F. Evenou (2006). Decolourization of textile wastewater was in the range 21–74% under solar irradiation, with COD removal rate between 0.2 and 0.9 g COD/h/m^2. These values are, however, strongly dependent upon the fine chemical structure of the dyes and the global composition of the wastewater. Performance prediction is therefore difficult but the results are encouraging for textile wastewater remediation. The increase of biodegradability is an additional positive factor, as it would improve the efficiency of a biological downstream treatment. No pH adjustment is necessary and wastewater at high pH can be treated directly after suspended solids removal.

CHAPTER 5

5. MATERIAL AND METHODS

This chapter lays emphasis on the materials and methods used during this research, including the chemicals, glassware instrument like the UV photo reactor, pH adjustment and analysis by UV-Vis Spectrophotometer, COD digester, weighing machine and procedures used to treat the compound with the UV/ZnO catalysis, Solar/ZnO UV/TiO_2 & Solar/TiO_2. The compilation of the varying pH of solution, ZnO dosages & TiO2 dosages and the varying UV and solar contact times for compound with varying concentrations.

5.1 Material

5.1.1 Procion Yellow Dye

Procion yellow dye solution produced from the textile industry near Ambala & it was used without further purification. Full scan of procion yellow dye was taken with the help of UV-vis spectrophotometer and maximum absorbance was observed at 402nm & 408nm. Molecular structure of procion yellow dye is illustrated in Fig-5.1. Procion yellow dye solution was prepared with the help of double distilled water.

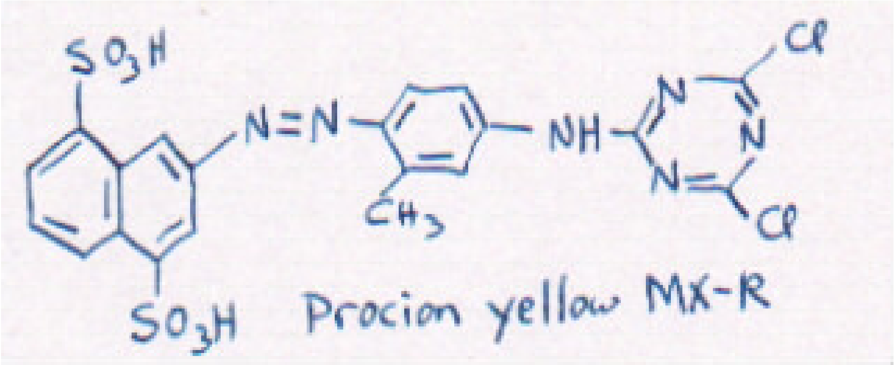


Fig-5.1 Structure of Procion Yellow MX-R

5.1.2 Reagent and chemical used

The photocatalyst ZnO and TiO_2 were procured from Degussa Company. Sodium hypochlorite and Hydrogen peroxide were used as oxidant. COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and Ferroin indicator. For all the experiments double distilled water were used. Different normality of (0.1, 1M) HCl and NaOH were used for adjustment of pH of compound solution.

5.2 Instrument used

5.2.1 pH meter

pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of NaOH (1M) and HCl (1M). Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study. (Fig-5.2)

Fig-5.2 pH meter

5.2.2 Magnetic stirrer

Magnetic stirrer was used during experimentation to solve the problem of mixing and titanium dioxide remains in suspension.

5.2.3 Aerator

Air is continuously supplied during experiments in UV reactor as well as solar experiments in order to provide sufficient DO to carry out oxidation of organic matter.

5.2.4 Photo reactor

Photocatalytic treatment of PYD solution was performed in batch experiments. For photocatalytic UV reactor was used which was rectangular having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of iron. Roof of the reactor was made up of wooden; seven UV tubes (36 Watt each) were attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Four magnetic stirrers were fitted in the reactor to carry out the photo catalytic reaction in slurry mode. Two different view of photoreactor are shown in Fig. -5.3 & 5.4

Fig- 5.3 Outer view of photo reactor

Fig-5.4 Photo reactor at lab level during photocatalytic treatment

5.2.5 Filtration

After photo catalytic treatment by photo reactor dye and effluent sample were filtered through syringe filters having milipore filters of 0.45 um pore size.

5.2.6 COD Digester

COD digester (Hatch) was used for the digestion of samples in the process of COD determination. (Fig-5.5)

Fig-5.5 COD digester

5.2.7 Reaction vessel

Glass bowls were used for the photocatalytic reactions having a capacity of 1 L.

5.2.8 Spectrophotometer

The spectrum was taken with UV-vis. Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer) at a wavelength of 408 nm in UV & 410 nm in Solar light (Fig-5.6).

Fig-5.6 Spectrophotometer

5.3 Methods

5.3.1 Preparation of solution

Procion Yellow Dye solution: The solutions were prepared by adding a definite amount of compound into a small amount of demonized water in a 1-liter Erlenmeyer flask and filling it to the mark with single distilled water. The flasks were covered with aluminum foil to avoid degradation by the laboratory fluorescent lights. Before the oxidation experiments could be performed, it was necessary to choose the appropriate concentration of compound solution. For most of the experiments, dye solutions of 100 ppm concentration were prepared by dissolving 0.100g in single distilled water and make the solution quantity to1 L.

5.3.2 Estimation of COD

COD was estimated as per the standard method No. 5220C; page No.5-14 from STANDARD METHODS for the examination of water and wastewater, 1989(17thedition).

5.3.4 Total dissolved solids (TDS)

TDS were estimated as per the standards methods No. 2540C; page No.2-74 of STANDARD METHODS for the examination of water and wastewater.

5.3.5 Total suspended solids (TSS)

TSS was estimated by method No. 2540 D, page No. 2-75 of STANDARDS METHODS for the examination of water and wastewater.

5.3.6 Electrical conductivity (EC)

EC is an important parameter to assess the wastewater quality. It is a measure of ionic concentration. It is an indicator of salinity also and measured in mS/cm.

Apparatus

The EC of effluent was estimated using conductivity meter.

5.3.7 UV intensity measurement

UV intensity was measured in the UV reactor with the help of radiometer. Radiometer was placed at different places from top with variation in distance from UV tubes such as top of the reactor, bottom of the reactor and middle of the reactor. It has been observed that the maximum UV intensity was at the middle of the UV reactor which was measured to be 25 W/m2.

5.3.8 Analysis for degradation

The degradation studies were conducted by measuring absorbance in UV/VIS spectrophotometer, having a wavelength range from 190-1100nm using a 1 cm quartz cell. The measurement of absorbance was done in a 4 ml quartz couvette. The scan speed is 200nm/min with a step of 1.0 nm. Wavelength resolution is 0.1 nm. Spectrophotometer is having both Tungsten and Deuterium lamp at operating temperature of 0-40oC.Full scan was treatment for the PYD solution.

5.4 Photocatalytic treatment

Photocatalytic treatment was done for PYD solution. The dye solution was treated and the various parameters like pH, catalyst dose, concentration of oxidant, initial concentration of compound were varied and optimized.

5.4.1 Degradation of Procion Yellow Dye

PYD solution of 100 ppm was prepared by the double distilled water. 200 ml of sample taken in glass bowl (1000ml quantity) and bowl was covered with transparent thin foil; air is also supplied by the aerator during experiments. Compound sample was treated in the presence of UV light in photo reactor for about 75min. Sample was withdrawn in every 15 min. filtered through the syringe filter and absorbance was taken in spectrophotometer. COD of samples was measured as per the standard methods. Initial pH of sample was checked and varied all the parameter to optimize the value of pH, catalyst dose, oxidant concentration and comparison of Photocatalytic activity with solar light. Experiments were also performed in solar light under optimized condition. All tests were repeated for getting the reproducibility of results. After the photocatalytic and solar photocatalytic treatment of wastewater (with optimized conditions), sample was filtered and it has been analyzed for COD, Color, pH, etc.

CHAPTER 6

6. RESULT AND DISCUSSIONS

The photocatalytic treatment using ZnO and TiO_2 catalyst were employed for the effective degradation of Procion yellow dye solution. A matrix of experimental variables was developed in which the catalyst dose, pH, UV exposure time, solar exposure time, and dye concentration were applied to dye solution.

6.1 Degradation of Procion Yellow Dye

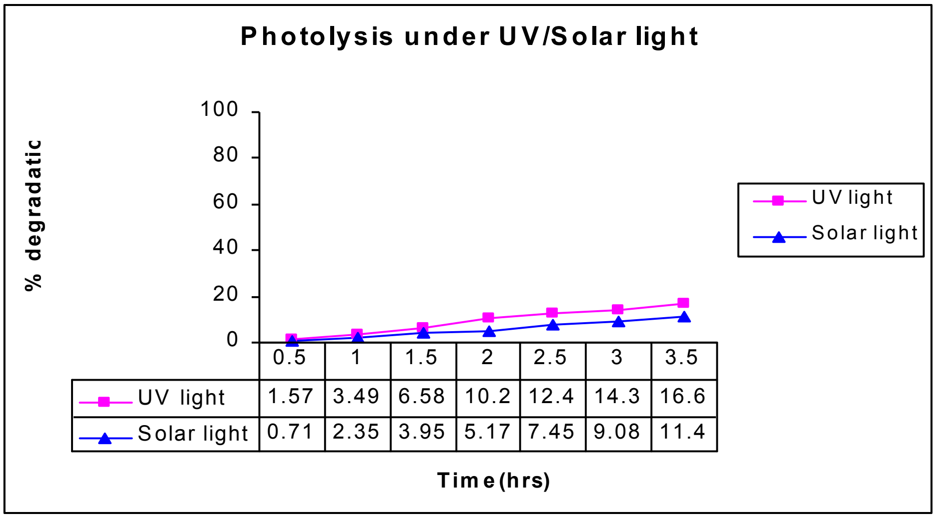
The procion yellow dye solution was subjected to photocatalytic treatment and the efficiency of treatment was investigated by altering parameters like pH, catalyst dose, UV intensity and variation of dye conc. as well as effect of effect of UV /Solar light, and UV intensity. Firstly dye sample was analyzed for some initial parameters. The values of various initial parameters of procion yellow dye before treatment are shown in Table 6.1

Table 6.1 Characteristics of Procion yellow dye

Sr. No.	Parameter	Value
1	pH	7.86
2	Conductivity(µ.moh/cm)	28
3	Turbidity(NTU)	44.95
4	Chloride(mg/l)	938.53
5	TS(mg/l)	0.227
6	TSS(mg/l)	0.211
7	TDS(mg/l)	0.016
8	COD(mg/l)	2000

6.1.1 Photolysis of Procion Yellow Dye

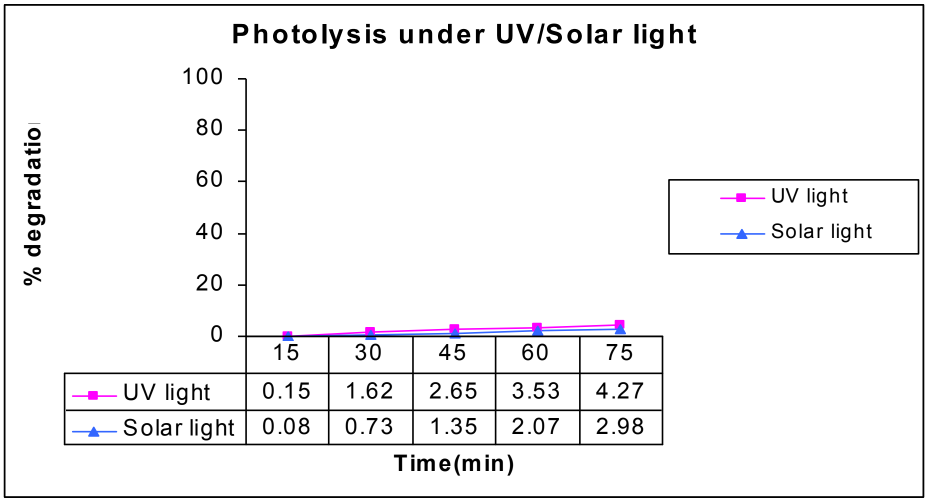
The degradation of Procion Yellow Dye was carried out in UV & Solar light alone without catalyst to asses the effect of light source on degradation efficiency. It observed that 16.6% & 11.4% degradation occurred without catalyst at natural pH after 3.5 hrs in UV and Solar light respectively (Fig-6.1).



	0.5	1	1.5	2	2.5	3	3.5
UV light	1.57	3.49	6.58	10.2	12.4	14.3	16.6
Solar light	0.71	2.35	3.95	5.17	7.45	9.08	11.4

Fig-6.1 Effect of UV/ Solar light without catalyst, Time= 3.5hrs

It is clear from graph (Fig-6.2) that 4.27 % and 2.98 % degradation at natural pH was observed in UV & Solar light respectively without catalyst which is quite in significantant.



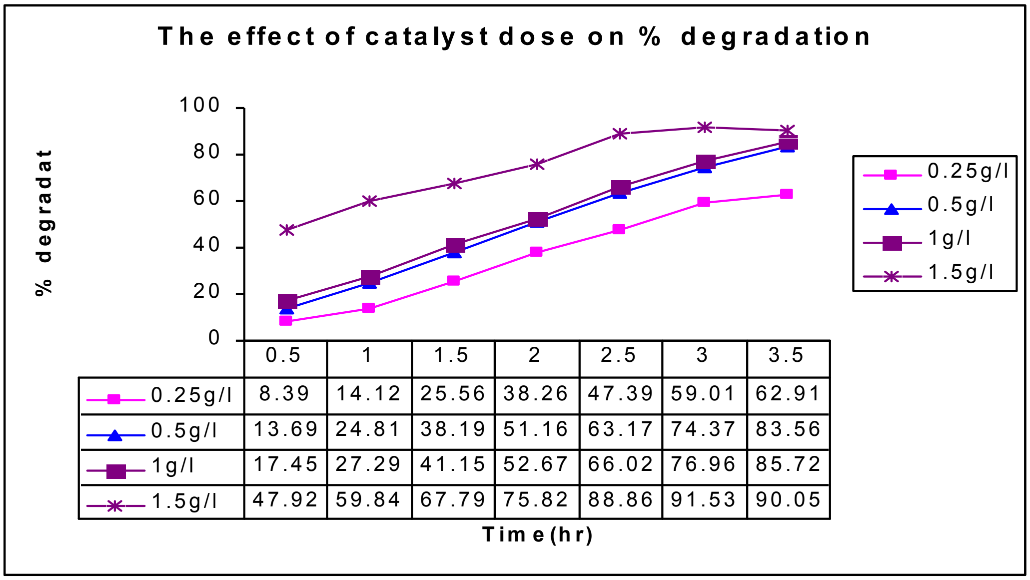
	15	30	45	60	75
UV light	0.15	1.62	2.65	3.53	4.27
Solar light	0.08	0.73	1.35	2.07	2.98

Fig-6.2 Effect of UV/ Solar light without catalyst, Time= 75min.

Kuo W.S and P.H.Ho, 2006 have reported the similar behavior during the photolysis of dye under ultraviolet & solar irradiation.

6.1.2 Effect of catalyst dose

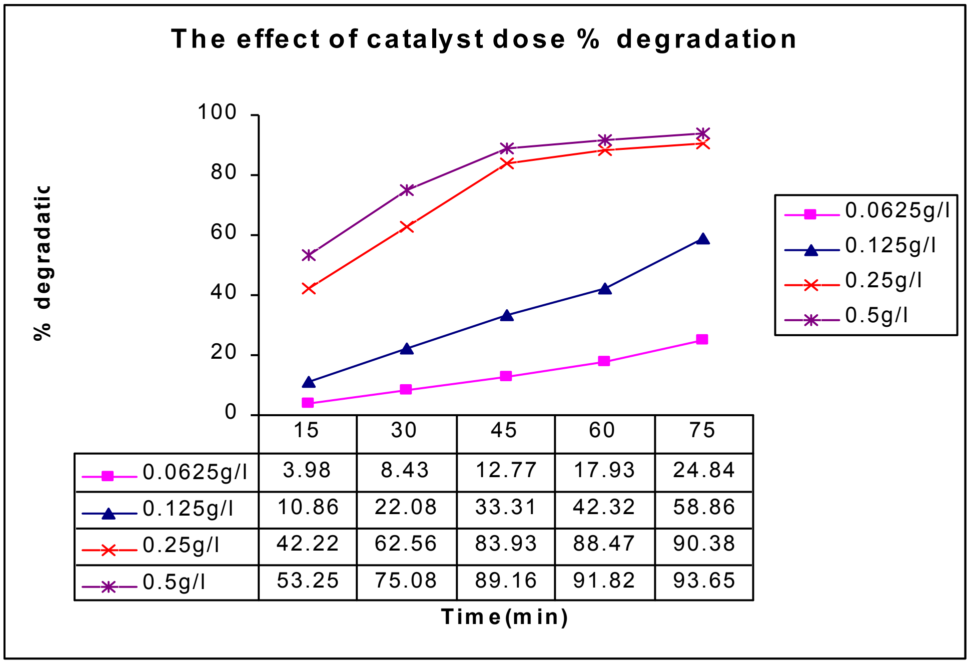
The catalyst dose is an important parameter which has strong influence on the degradation of dye solution. In order to determine the optimal amount of catalyst dose, a series of experiments were carried out using different concentrations of TiO_2 catalyst varying from 0.25 to 1.5g/L at natural pH (7.86) with 100 ppm PYD solution. And it was observed that as the concentration of catalyst increases from 0.25g/L to 1.5g/L, the percentage degradation varies (Fig-6.3). The maximum degradation 85.72 % has been observed at 1.0 g/l which is closed 83.56% to at 0.5 g/l in UV light after 3.5hr for the degradation of PYD solution (100 ppm). So 0.5g/l has been considered as an optimized dose of TiO_2 for degradation of PY Dye for subsequent analysis.



	0.5	1	1.5	2	2.5	3	3.5
0.25g/l	8.39	14.12	25.56	38.26	47.39	59.01	62.91
0.5g/l	13.69	24.81	38.19	51.16	63.17	74.37	83.56
1g/l	17.45	27.29	41.15	52.67	66.02	76.96	85.72
1.5g/l	47.92	59.84	67.79	75.82	88.86	91.53	90.05

Fig-6.3 Effect of catalyst dose (TiO_2) on Photocatalytic degradation of dye Irradiation time=3.5hr

After photo degradation TiO_2, catalytic activity of ZnO was compared. ZnO catalyst was used in slurry mode. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of ZnO catalyst varying from 0.0625 to 0.5g/L at natural pH with 100 ppm PYD solution. Figure(Fig-6.4) shows that as the concentration of catalyst increases from 0.0625g/L to 0.5g/L, the percentage degradation varies and the maximum degradation 93.6% has been observed at 0.5g/l which is closed to 90.38% at 0.25g/l in UV light for the degradation of PYD solution (100 ppm) after 75min. So 0.25g/l has been considered as an optimized dose of ZnO for degradation of PY Dye.



	15	30	45	60	75
0.0625g/l	3.98	8.43	12.77	17.93	24.84
0.125g/l	10.86	22.08	33.31	42.32	58.86
0.25g/l	42.22	62.56	83.93	88.47	90.38
0.5g/l	53.25	75.08	89.16	91.82	93.65

Fig-6.4 Effect of catalyst dose (ZnO) on photocatalytic degradation of Procion yellow dye, Irradiation time=75 min.

The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. ZnO is found is found to be more efficient in degrading PYD solution as compared to TiO_2.

Faisal et. al., (2005) have documented the effect of catalyst dose on two dyes acridine orange and ethidium bromide and observed that the degradation rate for the decomposition of both the dyes in the presence of TiO_2 Degussa P25 increases with the increase in catalyst concentration and a further increase in catalyst concentration leads to a decrease in degradation rate.

6.1.3 Influence of pH

Procion yellow dye solution in question has pH of 7.89 pH plays an important role in Photocatalytic oxidation processes because pH affects the production of hydroxyl radical which is powerful oxidizing agent. So pH was varied from 2.0 to 10 with optimized TiO_2 (0.5g/l) during experimentation and it was observed that the degradation of 84.8 % occurred at pH 8 which closed to 83.56% at natural pH (7.86) after 3.5 hr (fig-6.5). So natural pH has been considered as an optimized for degradation of PY Dye for subsequent analysis

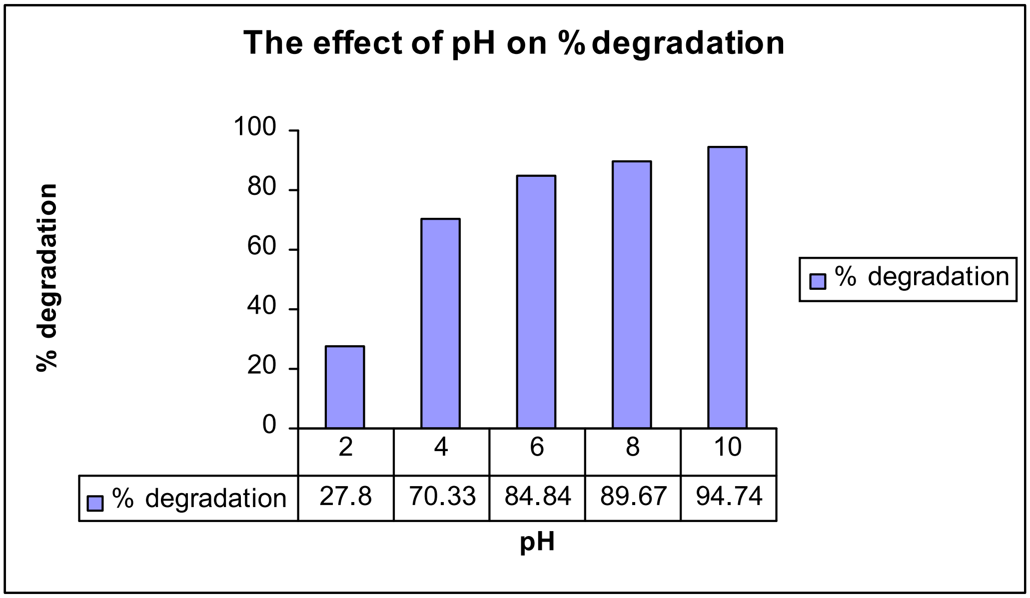


Fig-6.5 Effect of initial pH on Photocatalytic degradation of dye [TiO_2] = 0.5g/l, Irradiation time=3.50 hr

In case of Zinc oxide, pH was varied from 2.0 to 12 at 0.25g/l of catalyst dose during experimentation and it was observed that the degradation of 92.01 % occurred at pH 8 after 75 min (Fig-6.6). So on the basis of results obtained pH 8 was chosen to be optimum pH for photodegradtion. Since natural pH is 7.86 & degradation efficiency is almost same as that of pH 10.

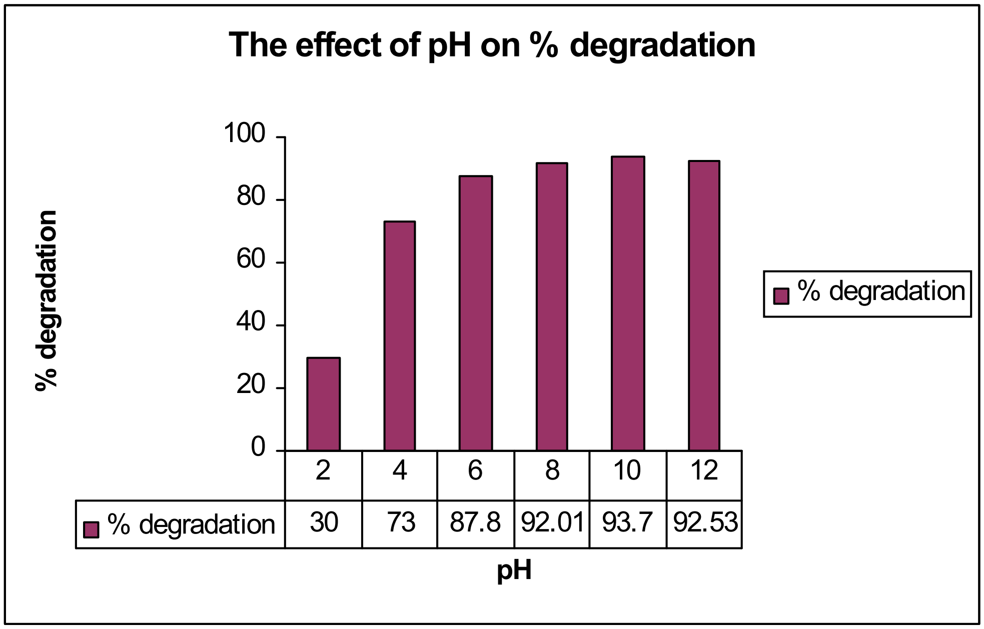


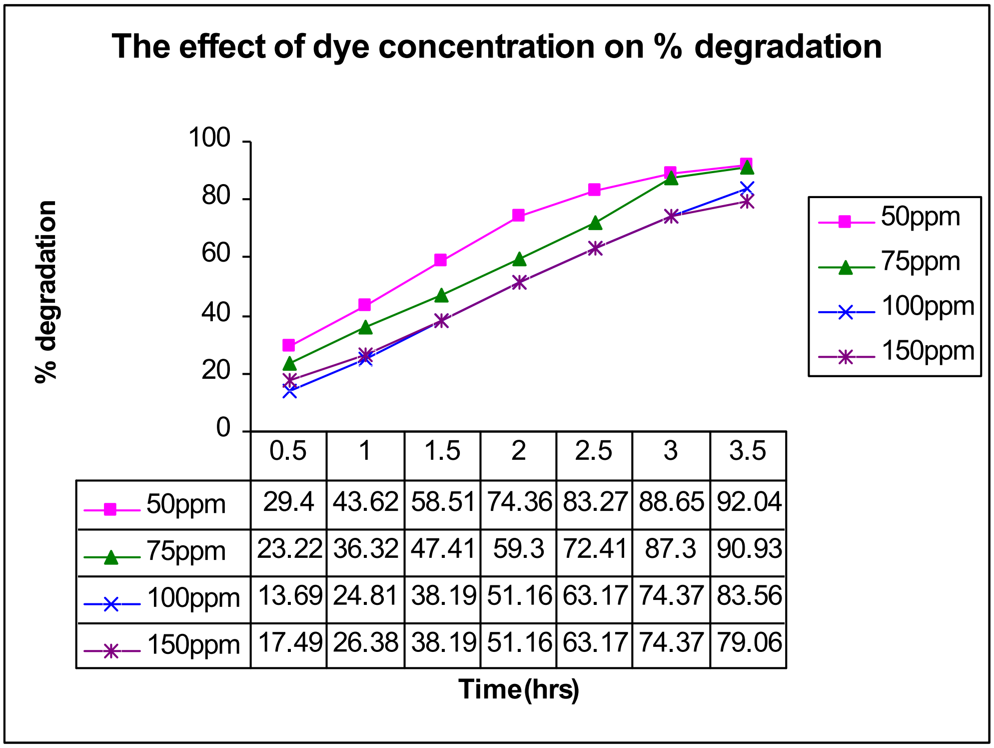
Fig-6.6 Effect of initial pH on photocatalytic degradation of Procion yellow dye [ZnO] =0.25 g/l, Irradiation time = 75min.

It is evident from the graph that ZnO is more efficient than TiO_2 because Zinc oxide consume less time and the final pH after photo catalytic treatment was 7.32 which is suitable for biological treatment as well as discharge of wastewater into the water bodies.

Literature survey also reveals that operating pH of solution significantly affects catalyst activity. Montaser Y. Ghalya et al. (2006) has been investigated the effect of pH in the range 2-10 for the degradation of simulated degradation of Maxoline Navy 2 RM basic dye in aqueous solution with TiO_2-A (pure anatase) as photocatalyst in slurry form. It is observed that elevating the pH of simulated, significantly improved the COD removal efficiency.

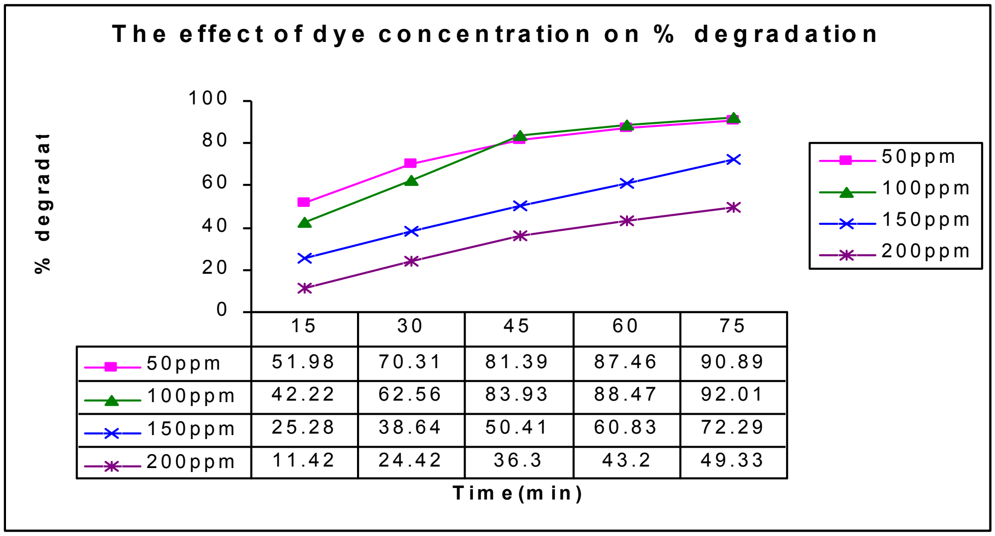
6.1.4 Effect of initial dye concentration

The influence of initial concentration of the PY Dye solution has been investigated on the photocatalytic degradation of compound after the optimization of pH and catalyst dose. The dye concentration was varied from 50 to 150 ppm, at natural pH and TiO_2 dose of 0.5g/L. It has been observed from the graph (Fig-6.7) that, the degradation was 83.56 % at 100ppm concentration.



	0.5	1	1.5	2	2.5	3	3.5
50ppm	29.4	43.62	58.51	74.36	83.27	88.65	92.04
75ppm	23.22	36.32	47.41	59.3	72.41	87.3	90.93
100ppm	13.69	24.81	38.19	51.16	63.17	74.37	83.56
150ppm	17.49	26.38	38.19	51.16	63.17	74.37	79.06

Fig-6.7 Effect of dye concentration on Photocatalytic degradation of dye at $[TiO_2]$ =0.50g/l & Irradiation time=3.50 hr



	15	30	45	60	75
50ppm	51.98	70.31	81.39	87.46	90.89
100ppm	42.22	62.56	83.93	88.47	92.01
150ppm	25.28	38.64	50.41	60.83	72.29
200ppm	11.42	24.42	36.3	43.2	49.33

Fig-6.8 Effect of dye concentration on photocatalytic degradation of Procion yellow dye [ZnO] =0.25 g/l, Irradiation time = 75min.

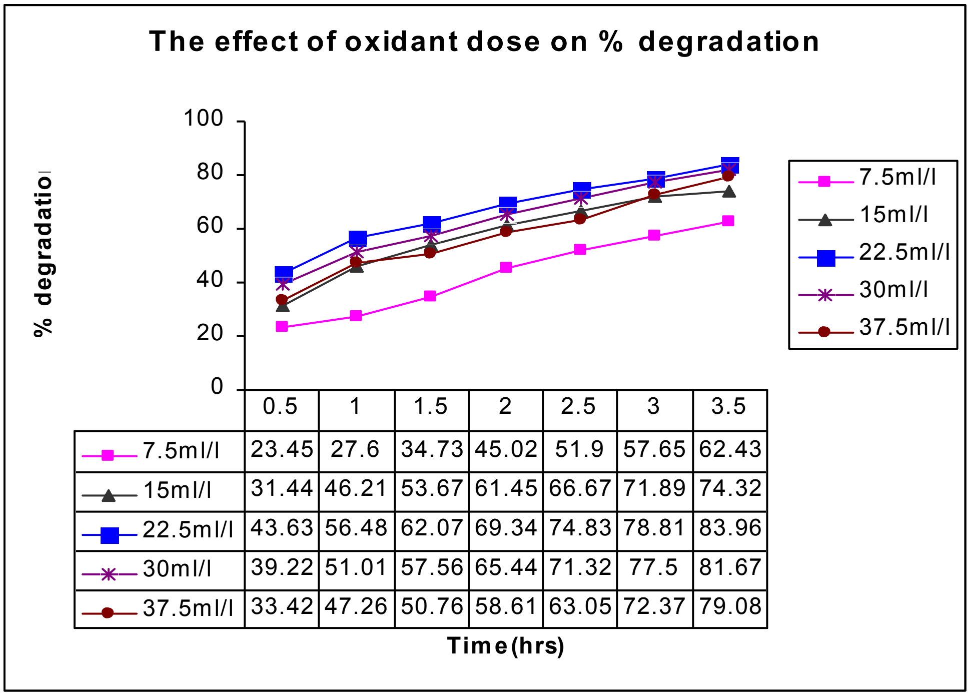
In order to optimize the ZnO dose the initial dye concentrations was varied during the photo catalytic treatment from 50 to 200 ppm, at 8 pH and catalyst dose of 0.25g/L. It has been observed from the graph (Fig-6.8) that increasing concentration of dye solution from 50 to 200 ppm decreases the percentage degradation rate and it was found that at 100ppm concentration, degradation was 92.01 %. For 200 ppm PYD concentration, percentage degradation was reduced to 49.39. The reason behind this behavior may be due to the increase in the extent of adsorption on the catalytic surface at necessary dye concentration which reduces the catalytic activity of ZnO. The increases in the PY Dye solution concentration also decrease the path length of photon entering into the dye solution. At high dye concentration a significant amount of UV-light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency

M.A. Barakat et.al(2010) studied on the adsorption and photodegradation of Procion yellow H-EXL dye over TiO_2 suspension. The photocatalytic process used the photogenerated holes and hydroxyl radicals as oxidizing species for the dye. Different parameters affecting the adsorption and photocatalytic degradation processes such as solution pH, initial dye concentration, and TiO_2 dosages were investigated. The dye removal % is inversely proportional to its concentration, the lower the dyes concentration, the higher the efficiency of dye removal. The efficiency values of both adsorption and photocatalytic degradation processes reached maximum value .

6.1.5 Effect of Oxidant concentration

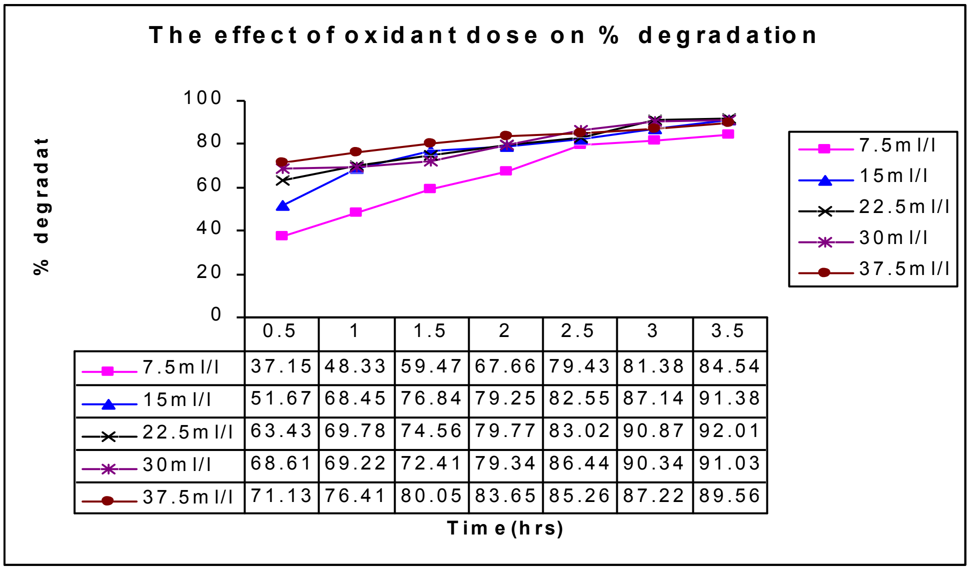
One possible way to increase the reaction rate is to increase the concentration of .OH radicals because these species are promoters of photocatalytic degradation. For the degradation of PYD solution, H_2O_2 was used as an oxidant along with TiO_2. The concentration of oxidant was varied from 7.5ml/l to 37.50ml/l at fixed TiO_2 dose (0.5g/l) and at natural pH during experimentation. Results show that 43.63% degradation occurred at 22.5ml/l of H_2O_2 while 12.69% degradation occurred without oxidant after 0.5 hrs. After 1.5 hrs, 62.07 % degradation with oxidant & 38.19% without oxidant occurred (fig6.9 & 6.3).Hence it is clear from the figure (Fig-6.9) that by addition of oxidant dose increase the rate of degradation of PY Dye solution.

The concentration of oxidant (NaOCl) was varied from 7.5ml/l to 37.50ml/l at fixed TiO_2 dose (0.5g/l) and at natural pH during experimentation. Results reveal, 63.43% degradation occurred at 22.5ml/l of NaOCl while 12.69% degradation occurred without oxidant after 0.5hrs. After 1.5 hrs 74.56% degradation with oxidant & 38.19% without oxidant occurred (Fig 6.10 & 6.3). It is clear from the figure (Fig-6.10) that the oxidant decreased reaction time of degradation of PY Dye solution.



	0.5	1	1.5	2	2.5	3	3.5
7.5ml/l	23.45	27.6	34.73	45.02	51.9	57.65	62.43
15ml/l	31.44	46.21	53.67	61.45	66.67	71.89	74.32
22.5ml/l	43.63	56.48	62.07	69.34	74.83	78.81	83.96
30ml/l	39.22	51.01	57.56	65.44	71.32	77.5	81.67
37.5ml/l	33.42	47.26	50.76	58.61	63.05	72.37	79.08

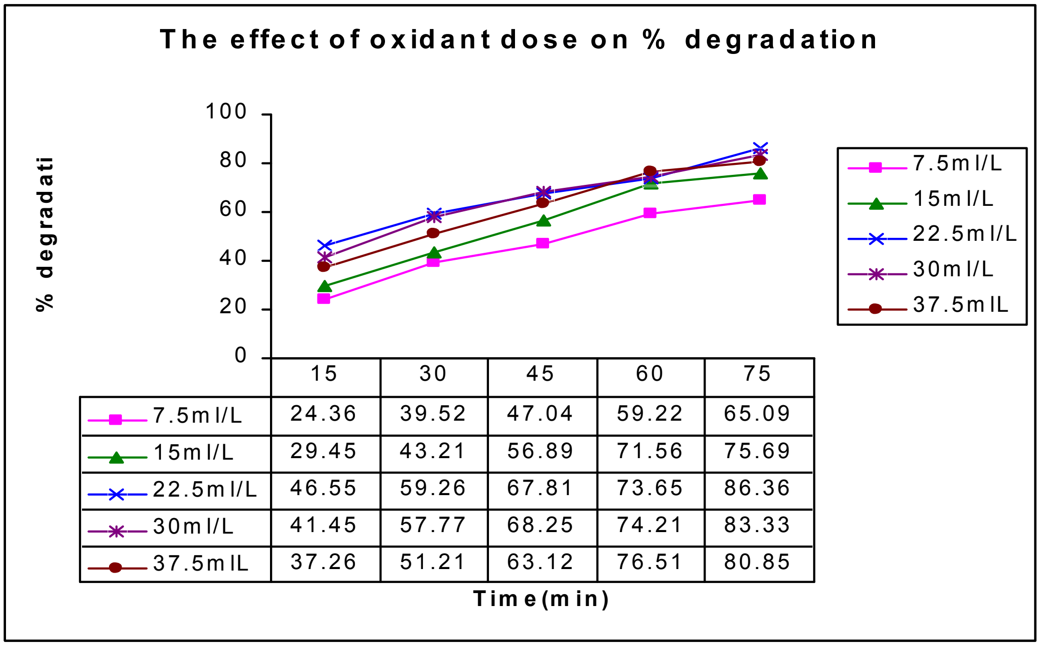
Fig-6.9 Effect of Oxidant dose (H_2O_2) on photocatalytic degradation of Procion yellow dye [TiO_2] =0.5 g/l, Irradiation time =3.5hrs.



	0.5	1	1.5	2	2.5	3	3.5
7.5ml/l	37.15	48.33	59.47	67.66	79.43	81.38	84.54
15ml/l	51.67	68.45	76.84	79.25	82.55	87.14	91.38
22.5ml/l	63.43	69.78	74.56	79.77	83.02	90.87	92.01
30ml/l	68.61	69.22	72.41	79.34	86.44	90.34	91.03
37.5ml/l	71.13	76.41	80.05	83.65	85.26	87.22	89.56

Fig-6.10 Effect of Oxidant dose (NaOCl) on photocatalytic degradation of Procion yellow dye [TiO_2] =0.5 g/l, Irradiation time =3.5hrs.

The concentration of oxidant (H_2O_2) was varied from 7.5ml/l to 37.50ml/l at fixed ZnO dose (0.25g/l) and at natural pH during experimentation. Results show that 86.36% degradation occurred at 22.5ml/l of (H_2O_2) while 92.01% degradation occurred without oxidant after 75min (Fig-6.11 & 6.4). Hence result indicates that the Hydrogen peroxide has no influences on rate of degradation of PY Dye solution.

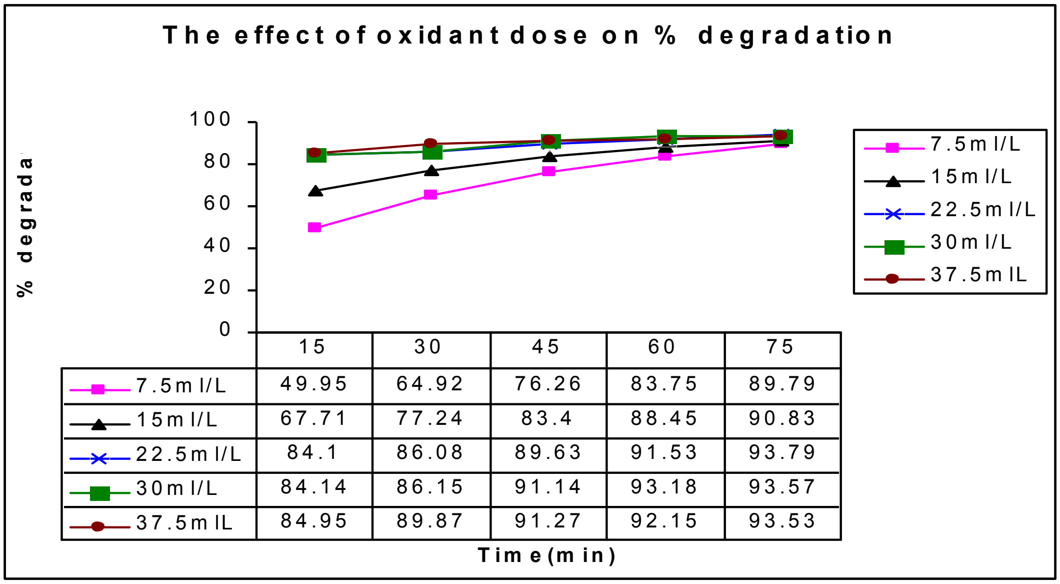


	15	30	45	60	75
7.5ml/L	24.36	39.52	47.04	59.22	65.09
15ml/L	29.45	43.21	56.89	71.56	75.69
22.5ml/L	46.55	59.26	67.81	73.65	86.36
30ml/L	41.45	57.77	68.25	74.21	83.33
37.5mlL	37.26	51.21	63.12	76.51	80.85

Fig-6.11 Effect of Oxidant dose (H_2O_2) on photocatalytic degradation of Procion yellow dye [ZnO] =0.25 g/l, pH=8, Irradiation time = 75min.

In case of ZnO with treatment of PYD solution, NaOCl was used as an oxidant. The concentration of oxidant was varied from 7.5ml/l to 37.50ml/l at fixed ZnO dose (0.25g/l) and at natural pH during experimentation. Results show that the 84.10% degradation occurred at 22.5ml/l of NaOCl while 42.22% degradation occurred without oxidant after 15 min. 89.63% degradation occurred with oxidant & 83.93% degradation occurred without oxidant after 45 min (Fig 6.12& 6.4). It is evident from the figure (fig 6.12) that the oxidant increased rate of degradation of PYD solution.

It is evident from graph (6.10 & 6.11) Sodium hypochlorite (NaOCl) is found is found to be more efficient in degrading PYD solution as compared to Hydrogen peroxide (H_2O_2).

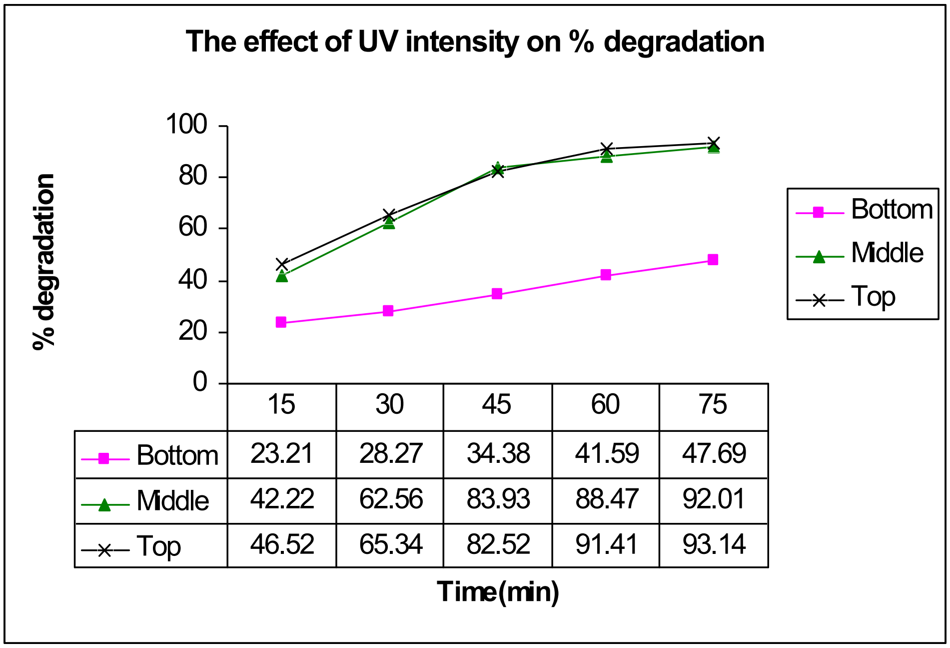


	15	30	45	60	75
■ 7.5ml/L	49.95	64.92	76.26	83.75	89.79
▲ 15ml/L	67.71	77.24	83.4	88.45	90.83
× 22.5ml/L	84.1	86.08	89.63	91.53	93.79
■ 30ml/L	84.14	86.15	91.14	93.18	93.57
● 37.5mIL	84.95	89.87	91.27	92.15	93.53

Fig-6.12 Effect of Oxidant dose (NaOCl) on photocatalytic degradation of Procion yellow dye [ZnO] =0.25 g/l, pH=8, Irradiation time = 75min.

6.1.6 Effect of UV intensity

The influence of UV light intensity on the degradation efficiency has been examined on PYD solution (100 ppm), at pH 8 and ZnO loading of 0.25 g/L. It is evident from the results that the percentage degradation increases with increase in the light intensity (Fig-6.13). The UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photo catalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced. The degradation efficiency is found to be maximum at the top & middle of the photo reactor where the intensity is maximum i.e. 25 W/m^2



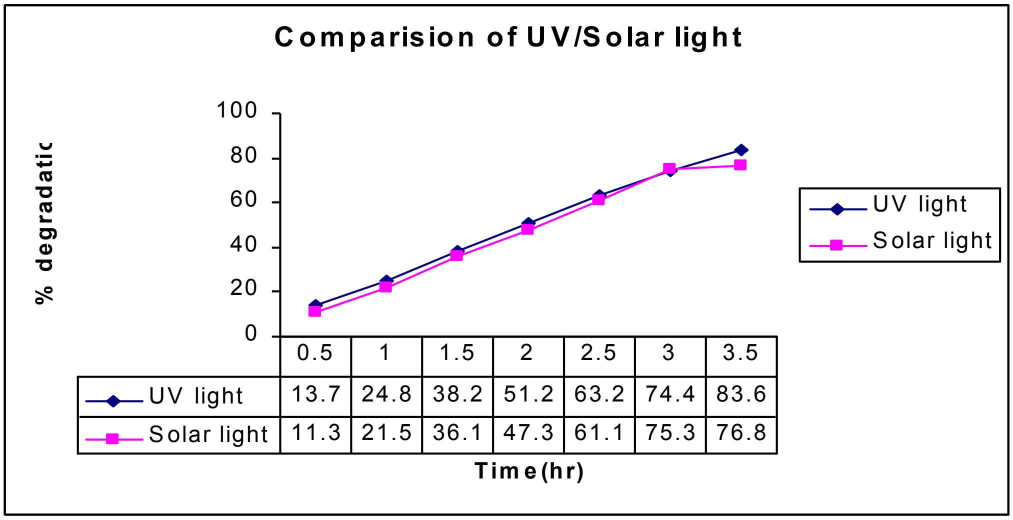
	15	30	45	60	75
Bottom	23.21	28.27	34.38	41.59	47.69
Middle	42.22	62.56	83.93	88.47	92.01
Top	46.52	65.34	82.52	91.41	93.14

Fig-6.13 Effect of UV intensity on photocatalytic degradation of Procion yellow dye [ZnO] =0.25 g/l, pH=8, Irradiation time = 75min.

6.1.7 Comparison of UV / Solar light:

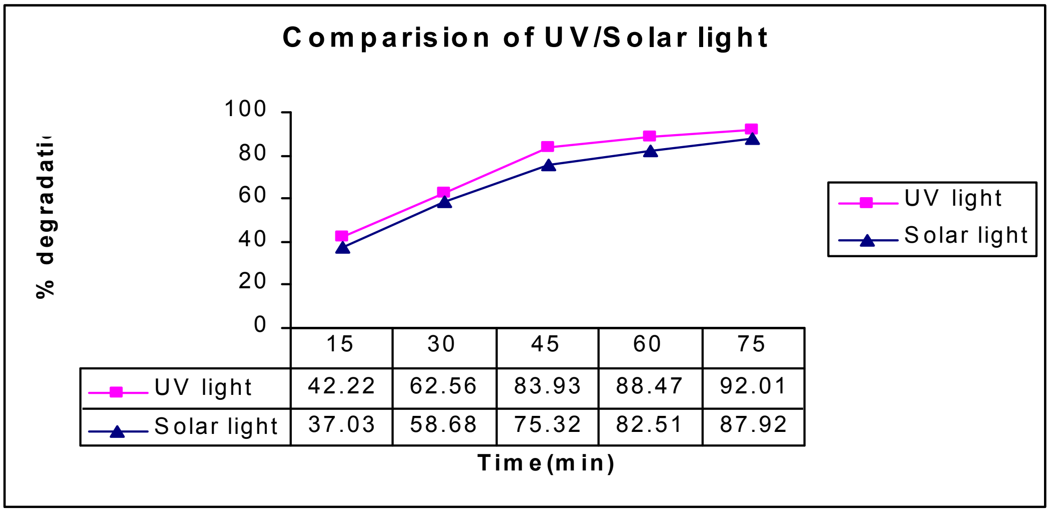
The effect of UV light on the degradation of PYD solution by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of compound solution in Solar / UV light. In case of TiO_2, the PYD (100ppm) solution containing TiO_2 (0.5g/l) was exposed to Solar & UV at natural pH. Fig shows the maximum degradation rate to be more in UV light as compared to Solar light (Fig-6.14).

In case of ZnO, the aqueous suspensions of ZnO (0.25 g/L) containing PY Dye solution (100ppm) was exposed to Solar & UV at pH 8.0 pH. Fig shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of dye solution under sunlight, and UV light source, respectively. The rate of degradation was found to be slightly more in the UV light in comparison to Solar light. After 75 min of reaction time the percentage degradation was 87.92 % in solar light and 92.01 % in UV light. It is evident from the graph (Fig-6.15) that percentage degradation of solar light is very close to UV light degradation so solar light can be efficiently used for the photocatalytic degradation of procion yellow dye.



Time (hr)	0.5	1	1.5	2	2.5	3	3.5
UV light	13.7	24.8	38.2	51.2	63.2	74.4	83.6
Solar light	11.3	21.5	36.1	47.3	61.1	75.3	76.8

Fig-6.14 Effect of UV/Solar light on Photocatalytic degradation of dye at natural pH (7.6), [TiO_2] =0.5g/l & Irradiation time=3.50 hr



Time (min)	15	30	45	60	75
UV light	42.22	62.56	83.93	88.47	92.01
Solar light	37.03	58.68	75.32	82.51	87.92

Fig-6.15 Effect of UV/Solar light on photo catalytic degradation of Procion yellow dye at 8 pH & [ZnO] =0.25 g/l, Irradiation time = 75min.

The photo oxidation Procion Yellow H-4R dyes, Bright Blue Remazol (blue reagent-19), Red Procion H-E7B, and the mixture of the two last dyes were investigated by Francisco A. P. Costa and Jorge Nozaki (2004). The efficiency of photooxidation were compared using hydrogen peroxide as a bleaching reagent, solar and ultraviolet radiation. The completely degradation of blue dye and a mixture of blue and red dyes were almost after 3 h, either by solar or ultraviolet radiation.

6.1.8 Dye characteristics after Photocatalytic Treatment

After the photocatalytic treatment of Procion yellow dye under optimized conditions i.e. at TiO_2 dose of 0.5g/l, operating natural pH, in UV light characterization was done. Table-6.2 & 6.3 shows the parameters analyzed after the 3.5hrs of photocatalytic treatment of PYD solution which depicts a major reduction in pollution load.

Tab-6.2 Characteristics of Procion yellow dye after Photocatalytic (UV light) Treatment under Optimized Condition with TiO_2 catalyst

Sr. No.	Parameter	Before Treatment	After Treatment	% Reduction
1	pH	7.89	7.4	------
2	Conductivity (µ.moh/cm)	28	11	60.71
3	Turbidity(NTU)	44.95	32.4	27.91
4	Chloride(mg/l)	938.53	473.98	49.50
5	COD(mg/l)	2000	1000	50

Tab-6.3 Characteristics of Procion yellow dye after Photocatalytic (Solar light) Treatment under Optimized Condition with TiO_2 catalyst

Sr. No.	Parameter	Before Treatment	After Treatment	% Reduction
1	pH	7.89	7.55	------
2	Conductivity (µ.moh/cm)	28	17	39.28
3	Turbidity(NTU)	44.95	28.5	36.59
4	Chloride(mg/l)	938.53	750.82	20
5	COD(mg/l)	2000	1200	40

These results show that complete degradation of dye solution has occurred. The other parameters like COD, Cl^- and EC as examined after treatment shows the 50 % reduction in COD, 49.50 % Cl^- reduction after 3.5hrs of reaction time in UV light. In the presence of solar light COD reduction was found to be 40 %, Cl^- reduction was 20% after 3.5hrs of treatment. Electrical conductivity and turbidity has been observed to decrease.

In case of treatment with Zinc Oxide (0.25g/l) and operating pH, in UV light characterization was done. Table- 6.4 & 6.5 shows the parameters analyzed after the

75min of photocatalytic treatment of PYD solution which depicts a major reduction in pollution load. These results show that complete degradation of dye solution has occurred. The other parameters like COD, Cl^- and EC as examined after treatment shows the 50% reduction in COD, 60% Cl^- reduction after 75min of reaction time. In the presence of solar light COD reduction was found to be 50 %, Cl^- reduction was 26% after 75 min of treatment. Electrical conductivity and turbidity has been observed to decrease.

Tab-6.4 Characteristics of Procion yellow dye after Photocatalytic (UV light) Treatment under Optimized Condition

Sr. No.	Parameter	Before Treatment	After Treatment	% Reduction
1	pH	7.89	7.32	------
2	Conductivity (µ.moh/cm)	28	9	67.85
3	Turbidity(NTU)	44.95	25.6	43.05
4	Chloride(mg/l)	938.53	375.41	60.00
5	COD(mg/l)	2000	800	60

Tab-6.5 Characteristics of Procion yellow dye after Photocatalytic (Solar light) Treatment under Optimized Condition

Sr. No.	Parameter	Before Treatment	After Treatment	% Reduction
1	pH	7.89	7.58	------
2	Conductivity (µ.moh/cm)	28	13	53.57
3	Turbidity(NTU)	44.95	24.5	45.49
4	Chloride(mg/l)	938.53	688.26	26.67
5	COD(mg/l)	2000	1000	50

CHAPTER 7

7 CONCLUSIONS

Photocatalysis is a promising technique, for the photodegradation of various hazardous chemicals that are present in industrial wastewater. Heterogeneous photocatalysis process is eco friendly way to reduce the pollution load of wastewater. This process has proved its superiority to other conventional methods of wastewater treatments, in the presence of biorecalcitrant compounds. It leads to complete destruction of hazardous contaminants and avoid transfer of pollutants from one phase to another. Photocatalytic process is expensive due to application of UV light and catalyst. India, being a tropical country, has plenty availability of sunlight so solar photocatalysis is an attractive and cost effective option for the application of this technology at industrial scale.

TiO_2 and ZnO are found to be efficient photocatalysts for the degradation of Procion Yellow Dye. The degradation experiments have been conducted and the best results were obtained when ZnO was used as a catalyst. Although ZnO is the most efficient catalyst but it has the disadvantage of undergoing photocorrosion under illumination in acidic conditions and high cost. The high photoreactivity of TiO_2 is due to the slow recombination of electron-hole pair and its large surface area.

In presence of TiO_2 catalyst, at optimized processes parameters, the COD of the treated sample after photcatalysis has been reduced from 2000 to 1000 mg/l in UV light and 2000mg/l to 1200mg/l in solar light was observed after 3.5 hrs.

It is evident from the results that end pH was 7.42 which is close to neutral. At optimized process parameters with ZnO, the COD of the treated sample in case of UV and solar photcatalysis has been reduced from 2000 to 800 mg/l in UV light and 2000mg/l to 1000mg/l in solar light was observed after 75 min. The reduction of COD was found to be slightly more in the in the presence of Zinc Oxide catalyst in comparison to Titanium Oxide catalyst. Moreover, the COD reduction & degradation effectively in case of ZnO over used early in 75 min where as in case of TiO_2 3.5 hrs of reaction time required for the degradation of dye.

In case of TiO_2, PY Dye has been degraded in the presence of UV/Solar light withTiO_2 dose (0.5g/l), at natural pH and irradiation time. Procion yellow dye, 83.6% degradation was achieved in UV at and 76.8% degradation was achieved in solar light.

Procion yellow dye has been successfully degraded in the presence of ZnO photocatalyst at an optimized to be 0.25g/l, at natural pH 92.01% degradation was achieved in UV light and 87.92% degradation was achieved in solar light It is evident from the results that solar light can be effectively used for the degradation Procion yellow dye solution. The rate of degradation was found to be slightly more in the UV light in comparison to Solar light. It is evident from the graph that percentage degradation of solar light is very close to UV light degradation. Hence, it can be concluded from the observations that solar photo catalysis can be suitably and cost effectively employed for the degradation of Procion yellow dye.

By addition of oxidant, the reaction time for the degradation of PY Dye solution decrease. It is evident from result Sodium hypochlorite (NaOCl) is found to be more efficient in degrading PY Dye solution as compared to Hydrogen peroxide (H_2O_2). H_2O_2 has no effect on degradation rate of Procion yellow dye solution when added ZnO.

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