STUDIES ON THE SOLAR ASSISTED ADVANCED OXIDATIVE TREATMENT OF PROCION BLUE DYE

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DECLARATION

I hereby declare that the work embodied in dissertation entitled, “**Studies on the solar assisted advanced oxidative treatment of Procion blue 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.

Ramanjot Kaur Sidhu

CERTIFICATE

This is to certify that the dissertation entitled, "**Studies on the solar assisted advanced oxidative treatment of procion blue dye**", is an authentic work carried out by Ramanjot Kaur Sidhu student of M.Tech. (Env.Sc. and Tech.) Thapar University, Patiala, during the year 2010 -2011, in partial fulfillments for the award of the Degree of Master of Technology and that the dissertation has not formed the basis for the award previously of any degree, associateship, fellowship or any other similar title to any other university or institute.

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RAMANJOT KAUR SIDHU

Abstract

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Considering both volumes discharged and effluent composition, the wastewater

generated by the textile industry is rated as one of the most polluting among all industrial sectors. About 1–20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. The release of these colored wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. Reactive dyes represent approximately 12% of the worldwide production of the commercialized synthetic dyes used. They are extensively used in the textile industry, fundamentally due to the capacity of their reactive groups to bind to textile fibers by covalent bond formation. This characteristic facilitates the interaction with the fiber and reduces energy consumption. The fixation efficiency of reactive dyes ranges between 60% and 90%. Consequently, substantial amounts (about 20%) of unfixed dyes are released in the wastewater, which causes major environmental problems. In view of the carcinogenic or mutagenic character of some reactive dyes, the deleterious effect of the color in the receiving waters, and the customary resistance of the effluents to biological degradation, the necessity of investigating new alternatives for the adequate treatment of this kind of residues are evident. The conventional technologies currently used to degrade the color of the dye-contaminated water include primary (adsorption, flocculation), secondary (biological methods), and chemical processes (chlorination, ozonization). However, these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to a new type of pollution, which needs further treatment. Advanced oxidation processes (AOPs) employing heterogeneous catalysis has emerged as potential destructive technology leading to the total mineralization of most of organic pollutants. Taking all these facts into consideration, in the present study, Procion Blue HERD (PB) dye was collected from textile mill. Photo degradation of PB dye was performed in specially designed reaction vessel and constant stirring of solution was ensured. Experiments were performed in slurry mode in both UV and solar light at optimized condition. The degradation of dye has been investigated in terms of change in color by measuring absorbance. Various process parameters like catalyst dose, pH, concentration of oxidant, initially pollutant concentration were varied and their effects have been analyzed.

The work done has been presented in five chapters. After introducing the problem in first chapter and giving brief account regarding treatment technologies in second chapter, the study begins with the literature review on photocatalyic degradation of various dyes in the third chapter. In the fourth chapter, experimental materials and methods have been discussed in detail. Results and their discussion of solar photocatalytic degradation of PBH dye compound in fifth chapter.

In the case of PB dye (25mg/L), TiO_2 dose was optimized to be 0.5 g/L, at operating pH of 4 along with oxidant concentration of 0.3 M (H_2O_2) .However with ZnO, parameters optimized were catalyst dose of 0.375g/L, pH 8 with oxidant concentration of 0.2M In case of PBH dye 86.23% degradation was achieved in solar light using TiO_2 (0.5g/L and pH 4) and with ZnO 97.61% degradation was achieved. With the addition of oxidant degradation rate increased in case of TiO_2 (86.94%) and there was reduction in degradation time with the addition of oxidant that was from 75 min to 45 min. with both catalysts.

The results of solar photo degradation of dye showed that solar photocatalysis using ZnO could be used as efficient and environmental friendly technique for degradation of PBH dye.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.0 Environment – definition and meaning

Word “environment” is most commonly used describing “natural” environment and means the sum of all living and non-living things that surround an organism, or group of organisms. Environment includes all elements, factors, and conditions that have some impact on growth and development of certain organism. Environment includes both biotic and abiotic factors that have influence on observed organism. Abiotic factors such as light, temperature, water, atmospheric gases combine with biotic factors (all surrounding living species).

1.1 Environmental Pollution: Pollution is the introduction of contaminants into a natural environment that causes instability, disorder, harm or discomfort to the ecosystem i.e. physical systems or living organisms. Pollution can take the form of chemical substances or energy, such as noise, heat, or light. Pollutants, the elements of pollution, can be foreign substances or energies, or naturally occurring; when naturally occurring, they are considered contaminants when they exceed natural levels.

1.1.1 Forms of pollution

- Air pollution, the release of chemicals and particulates into the atmosphere. Common gaseous air pollutants include carbon monoxide, sulfur dioxide, chlorofluorocarbons (CFCs) and nitrogen oxides produced by industry and motor vehicles. Photochemical ozone and smog are created as nitrogen oxides and hydrocarbons react to sunlight. Particulate matter, or fine dust is characterized by their micrometer size PM_{10} to $PM_{2.5}$.
- Light pollution, includes light trespass, over-illumination and astronomical interference.
- Littering
- Noise pollution, which encompasses roadway noise, aircraft noise, industrial noise as well as high-intensity sonar.
- Soil contamination occurs when chemicals are released by spill or underground leakage. Among the most significant soil contaminants are hydrocarbons, heavy metals, MTBE, herbicides, pesticides and chlorinated hydrocarbons.
- Radioactive contamination, resulting from 20th century activities in atomic physics, such as nuclear power generation and nuclear weapons research, manufacture and deployment. (See alpha emitters and actinides in the environment.)
- Thermal pollution, is a temperature change in natural water bodies caused by human influence, such as use of water as coolant in a power plant.
- Visual pollution, which can refer to the presence of overhead power lines, motorway billboards, scarred landforms (as from strip mining), open storage of trash or municipal solid waste.
- Water pollution, by the release of waste products and contaminants into surface runoff into river drainage systems, leaching into groundwater, liquid spills, wastewater discharges, eutrophication and littering.

1.1.2 Water pollution: 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 nonpoint source. Point sources of pollution occur when harmful substances are emitted directly into a body of water. The Exxon Valdez oil spill best illustrates a point source water pollution. A nonpoint 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. Nonpoint sources are much more difficult to control. Pollution arising from nonpoint sources accounts for a majority of the contaminants in streams and lakes.

1.1.3 Classifying water pollution: The major sources of water pollution can be classified as **municipal, industrial**, and **agricultural.**

Municipal is a waste type consisting of everyday items we consume and discard.

Industrial waste is a type of waste produced by industrial activity, such as that of factories, mills and mines.Toxic waste, chemical waste, Industrial solid waste and Municipal solid waste are designations of industrial waste

Agricultural Waste is waste produced at agricultural premises as a result of agricultural activity.

Agricultural premises are defined in the Agriculture Act 1947 as land used for: horticulture, fruit growing, seed growing, dairy farming, livestock breeding and keeping, grazing land, meadow land, osier land (growing willow), market gardens and nursery grounds.

1.2 Dyes and their intermediates, environmental concern

The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants *(Arslan et al., 2000; Sauer et al., 2002)* and nearly 10-15% of the dye is lost in the dyeing process and is released in the wastewater which is an important source of environmental contamination. Considerable amount of water is used for dyeing and finishing of fabrics in the textile industries. The wastewater from textile mills causes serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, chemicals which are dark in color leading to turbidity in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in textile water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and respiratory problems.

1.2.1 Dye types

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colors fall in this category.

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

Direct or **substantive dyeing** is normally carried out in a neutral or slightly alkaline dyebath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dyes are used on cotton paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

Vat dyes are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. "Cold" reactive dyes, such as Procion MX,Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton and other cellulose fibers at home or in the art studio.

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibres. In some cases, a dyeing temperature of 130 °Cis required, and a pressurised dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components. This method of dyeing cotton is declining in importance due to the toxic nature of the chemicals used.

Sulphur dyes are two parts "developed" dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chart reuse colour. This is after treated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulphur Black 1 is the largest selling dye by volume.

1.2.2 Discharge statistics of dye

Reactive dyes are known to form a covalent bond with the fibre in the dyeing process. This leads to favorable properties such as wash-fastness. However, unfixed dye reacts with water to form hydrolyzed or oxo-dye intermediate that has lost its bonding capacity and thus cannot be re-used. Therefore dye recovery is not an option with reactive dyes and the treatment process must lead to final destruction or disposal of these contaminants.

1.3 Wastewater Discharge Standards for Textile Industries

As environmental regulations become more stringent, many textile plants will be required to effluent treatment before discharging their wastewater into the environment. Research and development for the advancement of wastewater treatment are always under process, but existing discoloration and treatment methods in a textile industry has difficulty to remove the contaminants as per the discharge standards given in Table 1

Table 1: National Environmental Quality Standards (NEQS) of Textile Effluent

Parameters	**Values**
Temperature or Temperature increase	+<30ºC
Color (PCU)	7
pH value	6-10
BOD at 20ºC	80
COD	150
Total Suspended Solids (TSS)	150
Total Dissolved Solids (TDS)	3500
Oil and Grease	10
Ammonia (NH_3)	0.2
Nitrate	20
Phosphate	5
Chromium (total)	1.0
Sulphide	0.2
Calcium	200
Magnesium	200

Note: All values are in parts per million except pH(Source: CPCB)

1.4 Methods of treating waste water:

- ***Primary treatment*** consists of temporarily holding the sewage in a quiescent basin where heavy solids can settle to the bottom while oil, grease and lighter solids float to the surface. The settled and floating materials are removed and the remaining liquid may be discharged or subjected to secondary treatment.

- ***Secondary treatment*** removes dissolved and suspended biological matter. Secondary treatment is typically performed by indigenous, water-borne micro-organisms in a managed habitat. Secondary treatment may require a separation process to remove the micro-organisms from the treated water prior to discharge or tertiary treatment.
- ***Tertiary treatment*** is sometimes defined as anything more than primary and secondary treatment in order to allow rejection into a highly sensitive or fragile ecosystem (estuaries, low-flow rivers, coral reefs). Treated water is sometimes disinfected chemically or physically (for example, by lagoons and microfiltration) prior to discharge into a stream, river, bay, lagoon or wetland, or it can be used for the irrigation of a golf course, green way or park. If it is sufficiently clean, it can also be used for groundwater recharge or agricultural purposes.

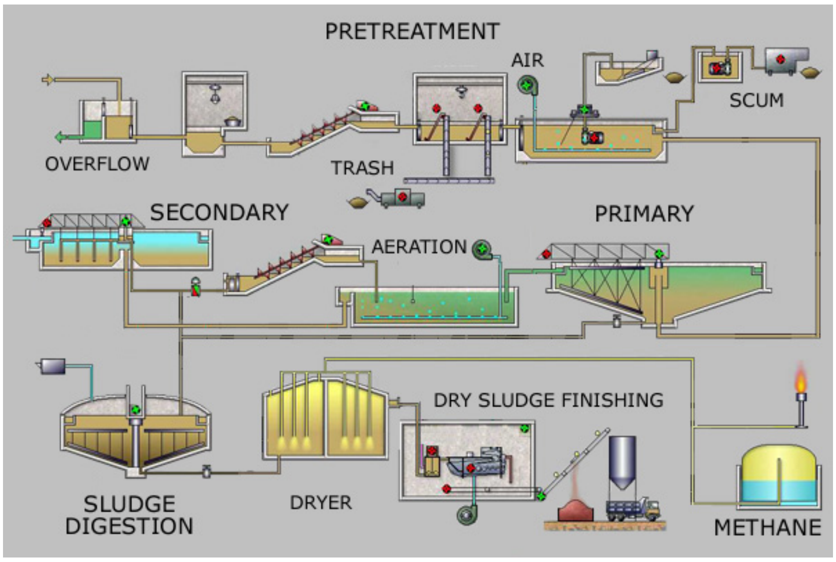


Fig 1.1 showing treatment of waste water

The European Union made out a list of dangerous compounds, considered as contaminants, to which constantly new substances are added ("black list" of the E.U., refer Table 2).

Table 2 Black list of chemical substances selected by the E.U. (Harrinson, 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.
Pesticides	Cyanide chloride, 2,4-dichlorophenoxyacetic acid and derivatives, 2,4,5 trichlorophenoxyacetic acid and derivatives, DDT, demeton, dichloroprope, dichlorvos, dimethoate, disulfoton, phenitrothion, phenthyon, linuron, malathion, MCPA, mecoprope, monolinuron, omethoate, parathion, phoxime, propanyl, pirazone, simacine, triazofos, trichlorofon, trifularin and derivatives.
Chloroanilines and nitrobenzenes	Monochloroanilines, 1-chloro-2,4 dinitrobenzene, dichloroaniline, 4-chloro-2-nitrobenzene, chloronitrobenzene, chloronitrotoluene, dichloronitrobenzene.
Polycyclic Aromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Inorganic substances	Arsenic and its compounds, cadmium and its compounds, mercury and its compounds.
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene, dichloromethane, dichloropropane, dichloropropanol, dichloropropene, ethyl benzene, toluene, tetrachloroethylene, trichloroethane, trichloroethylene.
Other	Benzidine, chloroacetic acid, chloroethanol, dibromomethane, dichlorobenzidine, dichloro-diisopropyl-ether, diethylamine, dimethylamine, isopropyl benzene, Tributylphosphate, trichlorotrifluoroethane, vinyl chloride, xilene.

In order to meet the stringent environmental standards, research on developing new, efficient and technologies for the degradation of biorecalcitrant organic compounds has drawn more attention. A one of the most promising treatment based on total degradation of hazardous organic compounds by using Advanced Oxidation Processes (AOP’s) has been reported. Advanced oxidation processes are chemical treatment given to such type of pollutants, which can not be treated by conventional treatment methods such as coagulation/flocculation, membrane separation (ultrafilteration, reverse osmosis) activated carbon adsorption and biological treatment. Advanced oxidation processes oxidize or mineralize the pollutants into their simpler forms, which are easily biodegradable and so it is facilitating their treatments in conventional processes, which are having an advantage of being cheaper than any other process. AOP’s can be homogeneous and heterogeneous in nature. Homogenous processes include simply the use of some chemicals/oxidation whereas heterogeneous processes employed some catalyst for the increasing rate of degradation process, known as heterogeneous advanced oxidation processes or catalytic oxidation processes. Theses processes are employed in the presence of UV, visible or solar light, for deriving the energy for oxidation of pollutants. So combination of theses process is called photocatalytic processes.

CHAPTER 2

TREATMENT TECHNOLOGIES

It was found that biological and coagulation flocculation treatments have proven insufficient to remove colour from a textile plant effluent. They produce an effluent characterized by relatively few COD, low biodegradability and high colour. The use of coagulants specific to colour removal applications may be considered. But although the removal efficiencies will improve slightly, the result will often remain insufficient. However with powdered activated carbon the performance will be enhanced somewhat. This option is viable only for solutions with low residual colour. The use of granular activated carbon would be costly the only alternatives remaining are AOPs and membrane processes. With membranes, the significant danger of clogging is there. So AOPs emerge as the most universal solution offering satisfactory efficiency. It produces an effluent with no colour, low COD, and suitable for discharge into the environment or return to the process.

2.1 Advanced Oxidation

Advanced chemical oxidation processes make use of (chemical) oxidants to reduce COD/BOD levels, and to remove both organic and oxidisable inorganic components. The processes can completely oxidize organic materials to carbon dioxide and water, although it is often not necessary to operate the processes to this level of treatment. A wide variety of advanced oxidation processes are available:

- Chemical oxidation processes using hydrogen peroxide, ozone, combined ozone & peroxide, hypochlorite, Fenton’s reagent etc.
- ultra-violet enhanced oxidation such as UV/ozone, UV/hydrogen peroxide, UV/air
- wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant)

2.2 Photocatalysis

The word photocatalysis is composed of two parts:

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

Hence, **photocatalysis** is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself.

2.2 Photocatalyst

Photo-Catalysis is defined as "acceleration by the presence of as catalyst". A catalyst does not change in itself or being consumed in the chemical reaction. This definition includes photosensitization, a process by which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitized. Chlorophyll of plants is a type of photocatalyst. Photocatalysis compared to photosynthesis, in which chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, photocatalysis creates strong oxidation agent to breakdown any organic matter to carbon dioxide and water in the presence of photocatalyst, light and water.

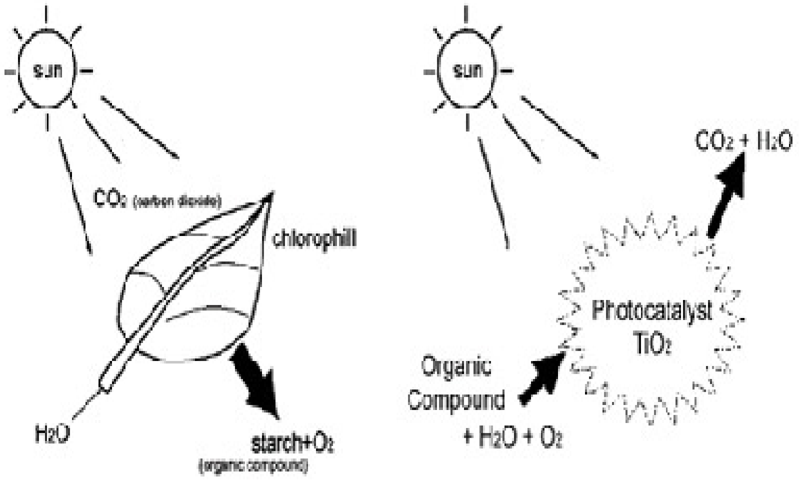


Fig-2.1 Photocatalysis v/s Photosynthesis

2.2.1 Mechanism

When photocatalyst absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e-) and positive-hole (h+) pair. This stage is referred as the semiconductor's ' **photo-excitation** ' state. The energy difference between the valence band and the conduction band is known as the ' **Band Gap** '. Wavelength of the light necessary for photo-excitation is: 1240 (Planck's constant, *h)* / 3.2 eV (band gap energy) = 388 m

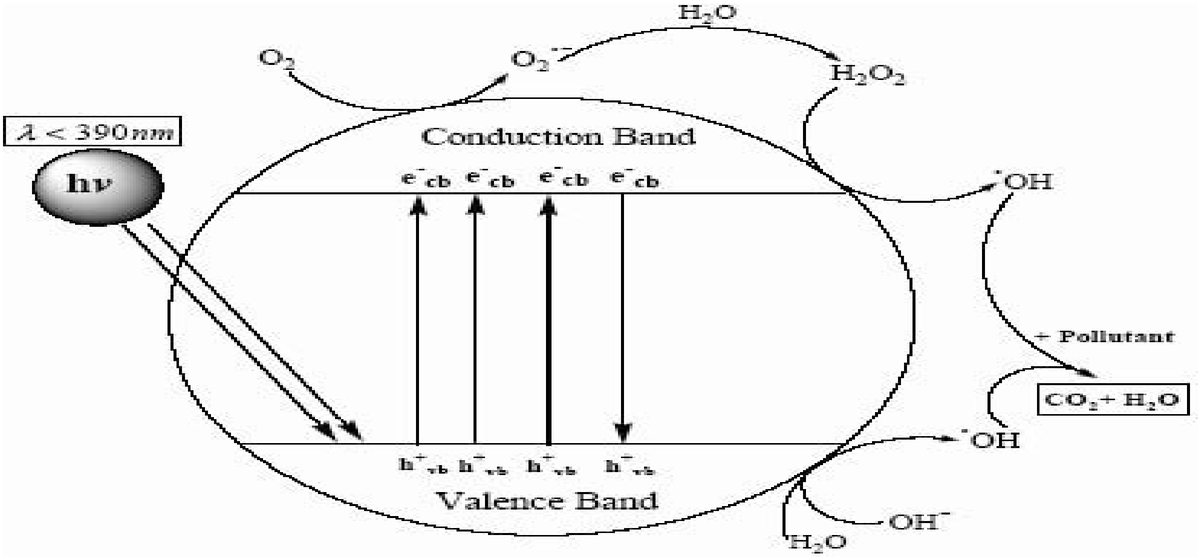


Fig-2.2 Mechanism of Photocatalysis

The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. It is a process in which the initial absorption of photons by a semiconductor, leads to the formation of electrons and holes. The band structure of the electronic energy levels of the semiconductor consists of the highest occupied band, called the valence band and the lowest unoccupied band called the conduction band separated by band gap energy (Ebg). The band gap energy falls in the UV-Visible region of the electromagnetic spectrum. Hence activation of the semiconductor surface (SC) with UV or Visible radiation results in the promotion of the valence band electron to the conduction band, generating electron(e^-) / hole (h^+) pairs.

$$SC \longrightarrow e^- + h^+ \qquad (1)$$

In aerated aqueous suspensions of the semiconductor in contact with organic substances, the photogenarated e^-/h^+ pairs initiate a series of redox reactions via a number of mechanisms which include:

1) Oxidation of adsorbed water molecules and hydroxyl ions by photo generated holes to give hydroxyl radicals

$$h^{+} + OH^{-} \longrightarrow OH \tag{2}$$

$$h^{+} + H_2O \longrightarrow OH^{\bullet} + H^{+} \tag{3}$$

2) Reduction of dissolved oxygen by the photo generated electrons to produce super oxide anions radicals, which in turn, can lead to generation of H_2O_2 through a series of redox reactions

$$O_2 + e^{-} \longrightarrow O_2^{-} \tag{4}$$

$$O_2^{-} + H^{+} \longrightarrow HO_2^{\bullet} \tag{5}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \tag{6}$$

$$^{\bullet}O_2^{-} + HO_2^{\bullet} \longrightarrow HO_2^{-} + O_2 \tag{7}$$

$$HO_2^{-} + H^{+} \longrightarrow H_2O_2 \tag{8}$$

The photo generated hydrogen peroxide undergoes further decomposition to yield hydroxyl radicals

$$H_2O_2 + O_2^{\cdot\,-} \longrightarrow {>}OH^{\cdot} + OH^{\cdot-} + O_2 \tag{9}$$

$$H_2O_2 + e^{-} \longrightarrow {>}OH^{\cdot} + OH^{-} \tag{10}$$

3) Direct participation of the holes and electrons in oxidation / reduction reactions

$$H_2O_2 + hv \longrightarrow .OH + .OH \tag{11}$$

$$\cdot OH + \text{dye} \xrightarrow{\hspace{3em}} \text{dye intermediate} \qquad (12)$$

$$\cdot OH + \text{dye intermediate} \xrightarrow{\hspace{3em}} CO_2 + H_2O + \text{end products} \qquad (13)$$

4) Formation of singlet oxygen, which can participate in oxidation reaction.

The primary oxidants, viz., hydroxyl radicals, super oxide anion radicals and H_2O_2 are strong, non selective oxidants, capable of initiating a series of oxidative degradation reaction of adsorbed organic molecules. Oxidation of organic compounds proceeds through a number of free radical reactions, producing a large number of intermediates, which in turn, undergo oxidative cleavage, ultimately resulting in the formation of carbon dioxide, water and inorganic ions.

2.2.2 Photocatalytic Oxidation

The most powerful advanced oxidation systems are based on the generation of hydroxyl radicals. The hydroxyl radical is an extremely powerful oxidation agent, second only to Fluorine in power (2.23 in Relative Oxidizing Power). Following is a listing of common chemical oxidants, placed in the order of their oxidizing strength:

Table 3 List of common chemical oxidants in order of their oxidizing strength

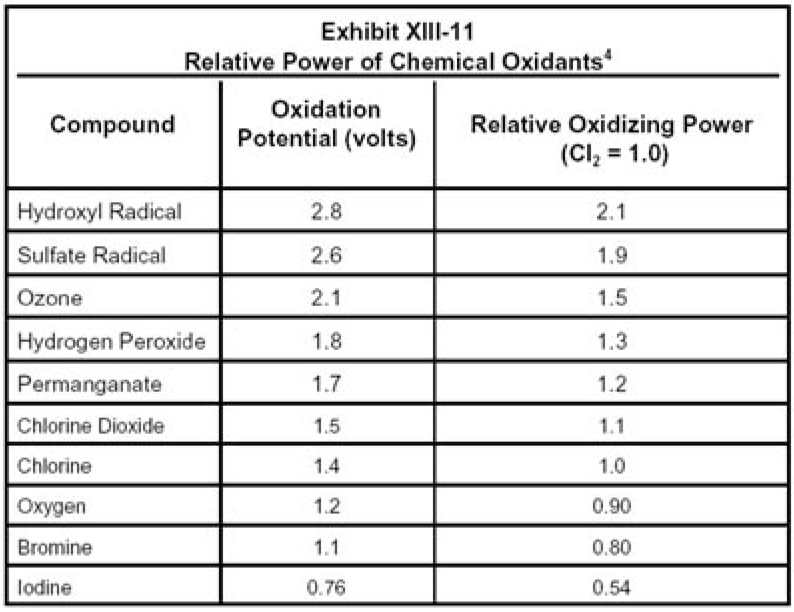


Exhibit XIII-11
Relative Power of Chemical Oxidants[4]

Compound	Oxidation Potential (volts)	Relative Oxidizing Power (Cl_2 = 1.0)
Hydroxyl Radical	2.8	2.1
Sulfate Radical	2.6	1.9
Ozone	2.1	1.5
Hydrogen Peroxide	1.8	1.3
Permanganate	1.7	1.2
Chlorine Dioxide	1.5	1.1
Chlorine	1.4	1.0
Oxygen	1.2	0.90
Bromine	1.1	0.80
Iodine	0.76	0.54

Utilizing the strong oxidation strength of hydroxyl radical, photocatalytic oxidation can effectively disinfect, deodorize, and purify air, water, and different surface area.

2.3 Types of Photocatalysis

2.3.1 Heterogeneous photocatalysis

2.3.2 Homogeneous photocatalysis

2.3.1 Heterogeneous photocatalysis

The concept of heterogeneous photocatalytic degradation is simple: the use under irradiation of a stable solid semiconductor for stimulating a reaction at the solid/solution interface. By definition, the solid can be recovered unchanged after many turnovers of the redox system. When a semiconductor is in contact with a liquid electrolyte solution containing a redox couple, charge transfer occurs across the interface to balance the potentials of the two phases. An electric field is formed at the surface of the semiconductor and the bands bend as the field forms from the bulk of the semiconductor towards the interface. During photoexcitation (a photon with appropriate energy is absorbed), band bending provides the conditions for carrier separation. In the case of semiconductor particles, there is no ohmic contact to extract the majority carriers and to transfer them by an external conductor to a second electrode. This means that the two charge carriers should react at the semiconductor/electrolyte interface with the species in solution. Under steady state conditions the amount of charge transferred to the electrolyte must be equal and opposite for the two types of carriers. The semiconductor mediated redox processes involve electron transfer across the interface. When electron/hole pairs are generated in a semiconductor particle, the electron moves away from the surface to the bulk of the semiconductor as the hole migrates towards the surface. If these charge carriers are separated fast enough they can be used for chemical reactions at the surface of the photocatalyst, i.e., for the oxidation or reduction of pollutants. TiO2/UV process is known to have many advantages:

- A large number of organic compounds dissolved or dispersed in water can be completely mineralized.
- The rate of reaction is relatively high if large surface area of the catalyst can be used.
- TiO_2 is available at a relatively modest price and can be recycled on a technical scale.
- UV lamps emitting in the spectral region required to initiate the photocatalytic oxidation are well known and are produced in various sizes.
- Absorption cross-section of TiO_2 can be improved by its surface modifications, e.g. by transition metal ion doping.

However, the only drawback in this method is that the liquid-solid separation is expensive, due to the formation of milky dispersions after mixing the powder catalyst in water. To solve this separation problem, fixed TiO_2 is prepared by coating a substrate with a TiO_2 solution and in most cases the catalyst shows a higher photocatalytic activity than the TiO_2 in slurry mode. However in general, the adherence of TiO_2 to support is not by a chemical bond and the heavier catalyst can be worn off easily. The various combined methods for •OH radical production mentioned above for the decomposition of a wide variety of organic contaminants have been reported by several authors and are of special interest since some of them can also use solar energy. A common problem of all the AOP’s is their high cost, mainly due to high demand of electrical energy for ozonizers and/or UV lamps. Application of solar irradiation to the photochemical process reduces cost but it is possible only for catalyzed homogeneous and heterogeneous reactions using iron ions and titanium dioxide respectively. These catalysts absorb at wavelengths of the solar spectrum while ozone and hydrogen peroxide do not absorb above 300 nm, which is the most important condition for the use of sunlight.

2.3.2 Homogeneous photocatalysis

The use of homogeneous photocatalysis (single-phase system) to treat contaminated waters dates back to the early 1970s. The first applications concerned the use of

UV/ozone and UV/H2O2. The use of UV light for photodegradation of pollutants can be classified into two principal areas:

Photo-oxidation-Light-driven oxidative processes principally initiated by hydroxyl radicals.

Direct photocatalysis-Light-driven processes where degradation proceeds following direct excitation of the pollutant by UV light.

Photooxidation involves the use of UV light plus an oxidant to generate radicals. The hydroxyl radicals then attack the organic pollutants to initiate oxidation.

Three major oxidants are used: hydrogen peroxide, ozone and Photo-Fenton reaction.

The use of hydrogen peroxide is now very common for the treatment of contaminated water due to several practical advantages: i) the H_2O_2 is available as an easily handled solution that can be diluted in water to give a wide range of concentrations; (ii) there are no air emissions; (iii) a high-quantum yield of hydroxyl radicals is generated (0.5). The major drawback is the low molar extinction coefficient, which means that in water with high UV absorption the fraction of light absorbed by H_2O_2 may be low unless very large concentrations are used. Furthermore, H_2O_2 absorption is very low in the Solar UV range (up 300 nm).

- Hydrogen peroxide (UV /H_2O_2)
- Ozone (UV /O_3)
- Hydrogen peroxide and Ozone (UV /O_3/H_2O_2)
- Photo-Fenton system (Fe+3 /H_2O_2)

2.4 Fundamental Parameters in Photocatalysis

The fundamental parameters related to heterogeneous photocatalysis are oxygen, pH, catalyst concentration, initial contaminant concentration and temperature.

2.4.1 Influence of Oxygen: - In semiconductor photocatalysis for water purification, the pollutants are usually organic and therefore the overall process can be summarized by the following equation

$$\text{Organic pollutant} + O_2 \xrightarrow{\qquad\qquad} CO_2 + H_2O + \text{mineral acids}$$

The concentration of oxygen also affects the reaction rate, which is faster when the partial pressure of oxygen (pO_2) in the atmosphere in contact with the water increases. In any case it seems that the difference between using air (pO_2 = 0.21 atm) or pure oxygen (pO_2=1 atm) is not drastic. In an industrial plant it would be purely a matter of economy of design. When all the oxygen contained in the water is consumed, photo decomposition of TOC comes to a halt. At the moment injected oxygen reaches the reactor photodecomposition continues. Therefore injection of pure O_2 becomes necessary in once through experiments at low flow rates. However at high flow rates or with recirculation, the addition of oxygen is not always necessary since the illumination time per pass is short. The water again recovers the oxygen consumed when it reaches the tank

2.4.2 pH influence: - The pH of the aqueous solution significantly affects TiO_2, including the charge of the particle and the size of the aggregates it forms. The pH at which the surface of an oxide is uncharged is defined as zero point discharge, which is 7 for TiO_2. Above and below this value, the catalyst is positively or negatively charged according to:

$$-TiOH_2^+ \longleftrightarrow TiOH + H^+$$

$$-TiOH \longleftrightarrow -TiO^- + H^+$$

The equilibrium constants of these reactions are pK $TiOH_2$ + = 2.4 and pK TiOH = 8, the abundance of all the species as a function of pH; TiOH >= 80% when 3<pH<10; -TiO- >=20% if pH >10; -$TiOH_2$+>=20% when pH<3.Under these conditions, the photo catalytic degradation of the ionisable organic compounds is affected by the pH. In many cases , a very important feature of photocatalysis is not taken into account when it is to be used for decontamination of water, is that during the reaction, a multitude of intermediate products are formed that may behave differently depending upon the pH of the solution. Therefore, a detailed analysis of the best pH conditions should include not only the initial substrate, but also the rest of the compounds produced during the process.

2.4.3 Influence of catalyst concentration: - Whether in static, slurry or dynamic flow photoreactors, the initial reaction rates were found to be directly proportional to catalyst mass. This indicates a truly heterogeneous catalytic regime. However, above a certain value, the reaction rate level off and becomes independent of catalyst mass. This limit depends on the geometry and working conditions of the photoreactor and is for a definite amount of TiO_2 in which all the particles, that is the entire surface exposed, are totally illuminated. When catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst mass has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons.

2.4.5 Initial Contaminant Concentration Influence: - As oxidation proceeds, less and less of the surface of the TiO_2 particles are covered as the contaminant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photo catalytic rate is to be expected with increasing illumination time.

2.4.6 Temperature Effect: - Because of photonic activation, photo catalytic systems do not require heating and operate at room temperature. The true activation energy Et is nil, whereas the apparent activation energy Ea is very low (a few kJ per mol) in the medium temperature range (20 to 80 ^{0}C). However at very low temperatures activity decreases and activation energy Ea becomes positive. By contrast at high temperatures for various types of photo catalytic reactions, the activity decreases and the apparent activation energy becomes negative.

In addition to these mechanical effects, other consequences of plant engineering must be considered. If temperature is high, the materials used for the plants should be temperature resistant and oxygen concentration in water decreases. Consequently, the optimum temperature is generally between 20 –80 ^{0}C. This absence of need for heating is attractive for photo catalytic reactions carried out in aqueous media and in particular for environmental purposes (photo catalytic water purification). There is no need to waste energy heating water that already possesses a high thermal capacity.

2.5 Applications of photocatalysis

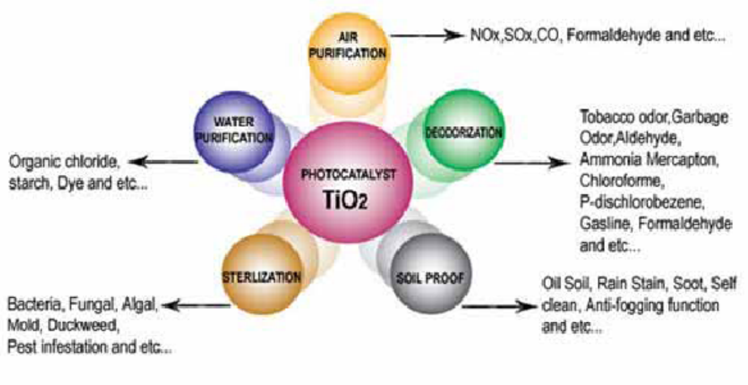


Fig-2.3 Applications of photocatalysis

2.5.1 Anti-Bacterial Effect

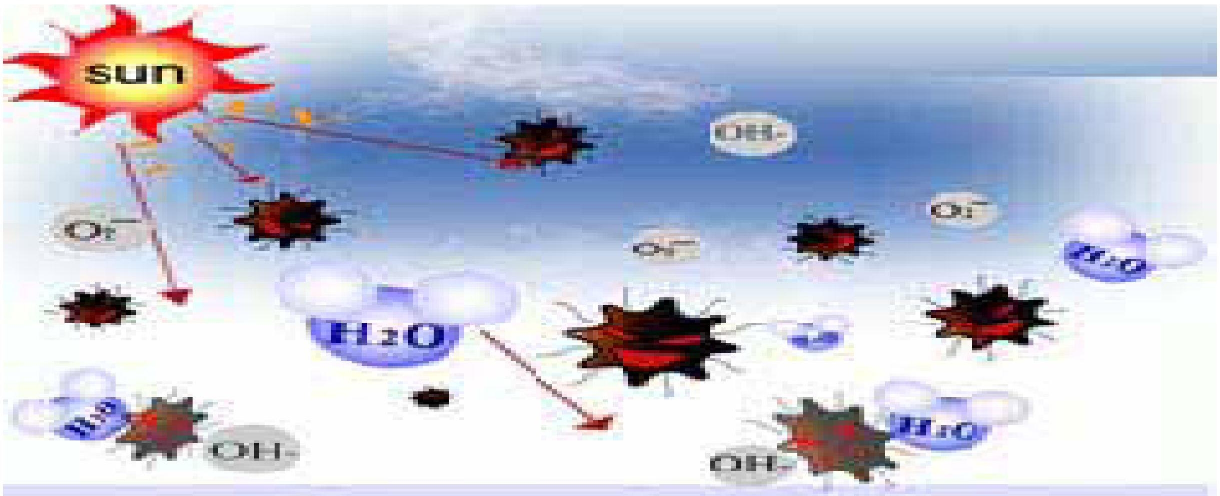
Photocatalyst does not only kill bacteria cells, but also decompose the cell itself. The titanium dioxide photocatalyst has been found to be more effective than any other antibacterial agent, because the photocatalytic reaction works even when there are cells covering the surface and while the bacteria are actively propagating. The end toxin produced at the death of cell is also expected to be decomposed by photocatalytic action. Titanium dioxide does not deteriorate and it shows a long-term anti-bacterial effect. Generally speaking, disinfections by titanium oxide is three times stronger than chlorine, and 1.5 times stronger than ozone.

2.5.2 Deodorizing Effect

On the deodorizing application, the hydroxyl radicals accelerate the breakdown of any Volatile Organic Compounds or VOCs by destroying the molecular bonds. This will help combine the organic gases to form a single molecule that is not harmful to humans thus enhance the air cleaning efficiency. Some of the examples of odor molecules are: Tobacco odor, formaldehyde, nitrogen dioxide, urine and fecal odor, gasoline, and many other hydro carbon molecules in the atmosphere. Air purifier with TiO_2 can prevent smoke and soil, pollen, bacteria, virus and harmful gas as well as seize the free bacteria in the air by filtering percentage of 99.9% with the help of the highly oxidizing effect of photocatalyst (TiO_2).

2.5.3 Air Purifying Effect

The photocatalytic reactivity of titanium oxides can be applied for the reduction or elimination of polluted compounds in air such as NOx, cigarette smoke, as well as volatile compounds arising from various construction materials. Also, high photocatalytic reactivity can be applied to protect lamp-houses and walls in tunneling, as well as to prevent white tents from becoming sooty and dark. Atmospheric constituents such as chlorofluorocarbons (CFCs) and CFC substitutes, greenhouse gases, and nitrogenous and sulfurous compounds undergo photochemical reactions either directly or indirectly in the presence of sunlight. In a polluted area, these pollutants can eventually be removed.



Photocatalyst TiO_2

Photocatalyst accelerates the oxidation process in the atmosphere and decomposes any air borne toxic organic matter.

2.5.4 Anti fogging, Self-Cleaning

Most of the exterior walls of buildings become soiled from automotive exhaust fumes, which contain oily components. When the original building materials are coated with a photocatalyst, a protective film of titanium provides the self-cleaning building by becoming antistatic, super oxidative, and hydrophilic. The hydrocarbon from automotive exhaust is oxidized and the dirt on the walls washes away with rainfall, keeping the building exterior clean at all times.

2.5.5 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.

2.6 Solar Chemistry

The dramatic increases in the cost of oil beginning in 1974 focussed attention on the need to develop alternative sources of energy. It has long been recognized that the sunlight falling on the earth's surface is more than adequate to supply all the energy that human activity requires. The challenge is to collect and convert this dilute and intermittent energy to forms that are convenient and economical or to use solar photons in place of those from lamps. Under these circumstances the growth and development of Solar Chemical Applications can be of special relevance.

These technologies can be divided in two main groups:

1. **Thermo chemical processes**: the solar radiation is converted into thermal energy that causes a chemical reaction. Such a chemical reaction is produced by thermal energy obtained from the sun for the general purpose of substituting fossil fuels.
2. **Photo chemical processes**: solar photons are directly absorbed by reactants and/or a catalyst causing a reaction. This path leads to a chemical reaction produced by the energy of the sun's photons, for the general purpose of carrying out new processes.
   The use of sunlight in photochemistry is to use solar photons as replacements for those from artificial sources. The goal in this case is to provide a cost effective and energy saving source of light to drive photochemical reactions with useful products. Photochemical reactions can be used to carry out a wide range of chemical synthesis ranging from simple to the complex. Processes of this type may start with more complex compounds than fuel producing or energy storage reactions and convert them to substances to which the photochemical step provides additional value or destroy harmful products.

2.6.1 Solar Irradiation

The spectrum of electromagnetic radiation striking the Earth's atmosphere is 100 to 10^6 nanometers (nm). This can be divided into five regions in increasing order of wavelengths:

- **Ultraviolet C** or (UVC) range, which spans a range of 100 to 280 nm. The term *ultraviolet* refers to the fact that the radiation is at higher frequency than violet light (and, hence also invisible to the human eye). Owing to absorption by the atmosphere very little reaches the Earth's surface (Lithosphere). This spectrum of radiation has germicidal properties, and is used in germicidal lamps.

- **Ultraviolet B** or (UVB) range spans 280 to 315 nm. It is also greatly absorbed by the atmosphere, and along with UVC is responsible for the photochemical reaction leading to the production of the Ozone layer.
- **Ultraviolet A** or (UVA) spans 315 to 400 nm. It has been traditionally held as less damaging to the DNA, and hence used in tanning and PUVA therapy for psoriasis.
- **Visible range** or **light** spans 380 to 780 nm. As the name suggests, it is this range that is visible to the naked human eye.
- **Infrared** range that spans 700 nm to 10^6 nm [1 (mm)]. It is responsible for an important part of the electromagnetic radiation that reaches the Earth. It is also divided into three types on the basis of wavelength:
  - Infrared-A: 700 nm to 1,400 nm
  - Infrared-B: 1,400 nm to 3,000 nm
  - Infrared-C: 3,000 nm to 1 mm.

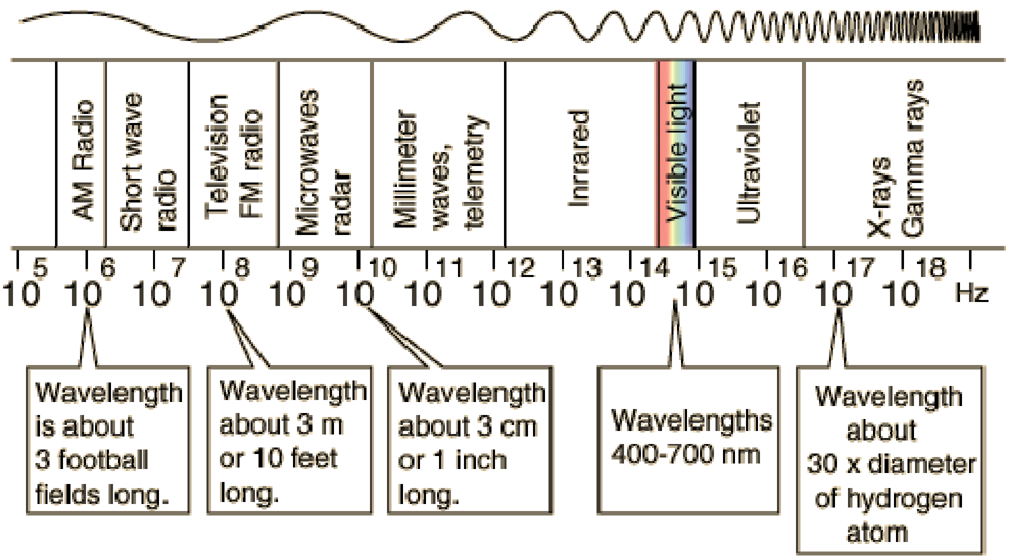
Table 4 gives approximate wavelengths, frequencies, and energies for selected regions of the electromagnetic spectrum.

Spectrum of Electromagnetic Radiation

Region	**Wavelength (Angstroms)**	**Wavelength (centimeters)**	**Frequency (Hz)**	**Energy (eV)**
Radio	$> 10^9$	> 10	$< 3 \times 10^9$	$< 10^{-5}$
Microwave	$10^9 - 10^6$	10 - 0.01	$3 \times 10^9 - 3 \times 10^{12}$	$10^{-5} - 0.01$
Infrared	$10^6 - 7000$	$0.01 - 7 \times 10^{-5}$	$3 \times 10^{12} - 4.3 \times 10^{14}$	0.01 - 2
Visible	7000 - 4000	$7 \times 10^{-5} - 4 \times 10^{-5}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$	2 - 3

Ultraviolet	4000 - 10	4×10^{-5} - 10^{-7}	7.5×10^{14} - 3×10^{17}	3 - 10^{3}
X-Rays	10 - 0.1	10^{-7} - 10^{-9}	3×10^{17} - 3×10^{19}	10^{3} - 10^{5}
Gamma Rays	< 0.1	< 10^{-9}	> 3×10^{19}	> 10^{5}

- (The notation "eV" stands for electron-volts, a common unit of energy measure in atomic physics.)



- **Fig-2.5 Electromagnetic spectrum**

Solar radiation and in particular its ultraviolet component is considered of interest being the existence of UV radiation the key of some heterogenous and homogenous photocatalytic processes.

Solar radiation gives all the energy coming from the sun, received by earth is approximately 1.7×10^{8} kWh year^{-1}. Beyond the atmosphere the wavelength of the radiation ranges from 0.2μ to 50μ, which reduces to 0.3μ to 3.0μ on reaching the earth due to absorption by atmospheric components.

Direct Radiation: The component of solar radiation reaching to earth without being absorbed or scattered is called direct radiation. It is minimum during cloudy days and maximum during clear days.

Diffused Radiation: the component of solar radiation reaching to earth without being dispersed is called diffused radiation. It is maximum during cloudy days and minimum during clear days.

Global Radiation: the sum of direct and diffused component of radiation is called global radiation it remains constant for a time.

Solar UV Radiation: it is a small fraction of total solar spectrum (3.5% to 8%). Global UV radiation increases with total global radiation. Average percentage of UV radiation with respect to total radiation in cloudy days is 2% higher than values on clear days.

2.7 Solar photocatalysis

The term photocatalysis implies the combination of photochemistry with catalysis. Both light and catalyst are necessary to achieve or to accelerate a chemical reaction. Photocatalysis may be defined as the “acceleration of a photo reaction by the presence of a catalyst”. Heterogeneous processes employ semiconductor slurries for catalysis, whereas homogeneous photochemistry is used in single phase system. Any mechanistic description of a photoreaction begins with the absorption of the photon, being sunlight the source of photons in **solar photocatalysis.** In the case of homogeneous photocatalytic processes, the interaction of a photon absorbing species, a substrate (contaminant) and light can lead to a chemical modification of the substrate. The photon absorbing species (**C**) is activated and accelerates the process by interacting through a state of excitation ($\mathbf{C}^*$). In the case of heterogeneous photocatalysis, the interaction of a photon produces the appearance of electron/ hole (e^- and h^+) pairs, the catalyst being a semiconductor (example titanium di oxide, zinc oxide etc.). In this case, the excited electrons are transferred to the reducible specimen (Ox_1) at the same time that the catalyst accepts electrons from the oxidizable specimen (Red_2) which occupies the holes. In both directions, the net flow of electrons is null and the catalyst remains unaltered.

2.8 Application of solar Photocatalysis to water treatment

UV light can be used in several ways but direct photolysis can occur only when the contaminant to be destroyed absorbs incident light efficiently in the case of UV/ ozone and UV/ hydrogen peroxide this does not happen. But here too, absorption by some sensitizer must initiate the reaction, and limited adsorption by the solute or the additive restricts efficiency. Furthermore, these mixers often still require large quantities of added oxidant. By contrast, in heterogeneous photocatalysis, dispersed solid particles absorb larger fractions of the UV spectrum efficiently and generate chemical oxidants in situ from dissolved oxygen or water. These advantages make heterogeneous photocatalysis a particularly attractive method for environmental detoxification. The most important features of this process making it applicable to the treatment of contaminated aqueous effluents are:

1. The process takes place at ambient temperature.
2. Oxidation of the substances into CO_2 is complete.
3. The oxygen necessary for the reaction is obtained from the atmosphere.
4. The catalyst is cheap, innocuous and can be reused.
5. The catalyst can be attached to different types of inert matrices.

Whenever different semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, TiO_2 has generally been demonstrated to be the most active. Only ZnO is as active as $TiO_{2.}$ TiO_2's strong resistance to chemical and photocorrosion, its safety and low cost, limits the choice of convenient alternatives. Furthermore, TiO_2 is of special interest since it can use natural or solar UV. This is because it has an appropriate energetic separation between its valence and conduction bands which can be surpassed by the energy content of a solar photon. Other semiconductor particles, example CdS absorb larger fractions of solar spectrum and can form chemically activated surface bond intermediates, but unfortunately these photocatalysts are degraded during the repeated catalytic cycles involved in heterogenous photocatalysis. Therefore degradation of the organic pollutants present in waste water using irradiated TiO_2 suspensions is the most promising processes.

$$TiO_2 \longrightarrow e^- + h^* + TiO_2 \qquad (1)$$

$$e^- + h^* + TiO_2 \longrightarrow TiO_2 + \text{heat and/ or hv'} \qquad (2)$$

$$(TiO^{IV} - O^{2-} - Ti^{IV})\text{- } OH_2 + h^+_{BV} \longrightarrow (TiO^{IV} - O^{2-} - Ti^{IV}) - OH + H^+ \qquad (3)$$

$$O_{2\,(ads)} + e^-_{BC} \longrightarrow O^-_{2(ads)} \qquad (4)$$

Hydroxyl radical (OH) is the main oxidizing specimen responsible for photooxidation of the majority of the organic compounds studied. The first effect, after absorption of UV radiation, is the generation of electron/ hole pairs, which are separated between the conduction and valence bands (Eq.1).

In order to avoid recombination of the pairs generated (Eq.2), if the dissolvent is oxidoreductively active (water) it also acts as a donor and acceptor of electrons (Eq.3).

In any case, it should be emphasized that even trapped electrons and holes can rapidly recombine on the surface of a particle (Eq.2). This can be partially avoided through the capture of electron by pre adsorbed molecular oxygen, forming a superoxide radical (Eq.4). Whatever the formation pathway, it is well known that O_2 and water are essential for photo oxidation with TiO_2. There is no degradation in the absence of either.

2.9 Solar Collector Technology Generalities

Traditionally, different solar collector systems have been classified depending on the level of concentration attained by them. The ***concentration ratio*** (**CR**) can be defined as the ratio of the collector aperture area to the absorber or reactor area. The ***aperture area*** is the area intercepting radiation and the absorber area is the area of the component (either fully illuminated or not) receiving concentrated solar radiation. This CR is directly related to the working system temperature and, according to this criterion; there are three types of collectors:

1. **Non concentrating or low-temperature, up to 150º C**
2. **Medium concentrating or medium temperature, from 150º C to 400º C**
3. **High concentrating or high temperature, over 400º C**

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

2.9.1 **Non-concentrating solar collectors** are static and non-solar-tracking. Usually, they are flat plates, often aimed at the sun at a specific tilt, depending on the geographic location. Their main advantage is their simplicity and low cost. An example is domestic hot water technology.

2.9.2 **Medium concentrating solar collectors** concentrate sunlight between 5 and 50 times, so continuous tracking of the sun is required. Parabolic Trough Collectors (PTC) and holographic collectors (Fresnel lenses) are in this group. The first have a parabolic reflecting surface which concentrates the radiation on a tubular receiver located in the focus of the parabola. They may be one-axis tracking, either azimuth (east-west movement around a north-south-oriented axis) or elevation (north-south movement around an east-west-oriented axis), or two-axis tracking (azimuth + elevation). Fresnel lens collectors consist of refracting surfaces (similar to convex lenses) which deviate the radiation at the same time they concentrate it onto a focus.

2.9.3 High concentrating collectors have a focal point instead of a linear focus and are based on paraboloid with solar tracking. Typical concentration ratios are in the range of 100 to 10000 and precision optical elements are required. They include parabolic dishes and solar furnaces.

2.10 Objective of present study

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

- Solar photocatalytic treatment of Procion blue dye
- Effect of variables on degradation efficiency and their optimization
- Comparison of different catalysts activity

Chapter – 3

Review of literature

Wastewater generated from different industries is posing a great threat not only to mankind but also to the landmass fertility as well as natural flora and fauna. *(Vincenzo Augugliaro et al., 2006)***.** Textile manufacturing involves several processes (e.g. sizing of fibers, scouring, de-sizing, bleaching, rinsing, mercerizing, dyeing and finishing) which generate large quantities of wastewaters. These effluents are highly variable in composition with relatively low biological oxygen demand (BOD) and high chemical oxygen demand (COD) contents. The most typical characteristic of textile wastewaters is their strong color due to residual dyes. It is estimated that approximately 15% of the total production of colorants is lost during synthesis and processing and the main source of this loss is to be found in wastewaters due to incomplete exhaustion. Dye molecules often receive the largest attention due to their color, as well as the toxicity of some of the raw materials used to synthesize dyes (e.g. certain aromatic amines), although dyes are often not the largest contributor to the wastewater . Dyes concentration in wastewaters is usually lower than any other chemical found in these wastewaters, but due to their strong color they are visible even at very low concentrations, thus causing serious aesthetic and pollution problems in wastewater disposal *(Pekakis et al., 2006)*. In order to meet the stringent international standards, treatment of textile wastewater is mandatory A survey of literature was carried out to know the latest advancements in the field of photocatalysis for the treatment of dyes and textile wastewater

Costa et al.,2004 investigated the photooxidation of textile dyes Yellow Procion H-4R, Bright Blue Remazol (blue reagent-19), Red Procion H- E7B, and the mixture of the two last dyes and compared the efficiency of photooxidation using hydrogen peroxide (30%) as a bleaching reagent, solar and ultraviolet radiation, common glass borosilicate, quartz assay tubes, and no solid catalysts. He found that the colour of blue dye and a mixture of blue and red dyes were almost completely removed after 3 h, either by solar or ultraviolet radiation. The best results of colour removal (93%) for the red and yellow dyestuffs were obtained only after 6 h, using quartz tubes, hydrogen peroxide and ultraviolet radiation**.**

Application of TiO_2 film to solar photocatalysis of organic dyes, including Methylene Blue (MB) (l, 540 nm) and RY145 (l maxmax, 420 nm), was investigated by *Kuo et al., 2005*. It was found that after 6-h solar irradiation, the extent of color degradation of dyes using solar photocatalytic system without TiO_2 film was quite limited. The color removal percentage for MB, RR195, and RY145 was found to be 23.3, _9.3, and _20.7%, respectively, resulting from competitions between the photosensitizing reaction and formation of colored intermediates during solar irradiation. However, as TiO_2 film was applied, the color degradation capability solar photocatalytic system was significantly improved, in spite of the fact that only approximately 7% of solar irradiation belongs to the UV region. The color removal percentage for MB, RR195, and RY145 was up to 93.6%, 85.3%, and 71.1%, respectively, after 6-h irradiation. It was found that such a solar photocatalytic system immobilized with TiO_2 film, both the maximum absorbance wavelength of the dye and the adsorbability of the dye on TiO_2 film played significant roles on the rate and efficiency of color removal of the dye solutions.. Color removal rate of MB was almost twice of that of RY145. Accordingly, the photocatalytic degradation process using solar light as an irradiation source, and, 660 nm), RR195 (l2 max immobilized TiO_2 as a photocatalyst, showed potential application for the decolourization of wastewater**.**

Nanosized coupled ZnO/SnO_2 photocatalysts with different Sn contents were prepared using the coprecipitation method, and characterized by X-ray diffraction, specific surface area and UV-Vis diffuse reflectance spectroscopy. The phases, mean grain sizes and band gap energy of the coupled ZnO/SnO_2 photocatalysts varied with the Sn contents and the calcination temperatures. The Photocatalytic activities of the coupled ZnO/SnO_2 photocatalysts, evaluated using the photodegradation of methyl orange as a probe reaction, were also found to be related to the calcination temperatures and the Sn contents. The photocatalytic activities of the coupled ZnO/SnO_2 photocatalysts decreased with the increasing calcination temperatures. The maximum photocatalytic activity of the coupled ZnO/SnO_2 photocatalyst, which is about 1.3 times the photocatalytic activity of ZnO and 21.3 times that of SnO2, was observed with a Sn content of 33.3 mol% under calcination at 500◦C for 10 h. The enhancement of the photocatalytic activity might arise from the hetero-junctions ZnO/SnO_2 in the coupled oxides. The photo-stability of the ZnO/SnO_2 photocatalyst was also studied *(Wang et al., 2004)*

M. Muruganandham et. al., 2006 evaluated the decolorisation of an azo dye Reactive Yellow 14 (RY14) by three advanced oxidation processes viz., solar/TiO_2, solar/H_2O_2 and solar/H_2O_2/Fe^{2+} (photo-Fenton). The effects of various experimental parameters such as pH, dye concentration, light intensity on the solar decolorisation was studied. The photo decolorisation efficiencies with solar irradiation are comparable to UV irradiation. *I. A. Salem et. al., 2000* studied the color removal of the cationic dye methylene blue by complete oxidative mineralization with H_2O_2 catalyzed with some supported alumina catalysts. The rate of color removal depends on the concentration of reactants, pH, and ionic strength, and surfactant concentration. The supported catalysts are very stable and can be used for several times. *Zulkarnain Zainal et.al.,2005* photodegradation were carried out of methylene blue (MB), methyl orange (MO), indigo carmine (IC), chicago sky blue 6B (CSB), and mixed dye (MD, mixture of the four mentioned single dye using glass coated titanium dioxide thin film as photo catalyst. As each photo degradation system is pH dependent. The characteristic of the photocatalyst was investigated using X-ray diffractometer (XRD).

The degradation of X6G (C.I. Reactive Yellow 2), commonly used as textile dye, can be photocatalyzed by ITO and TiO_2 thin films. The degradation can be completed in the order of minutes at optimal operational parameters. Using advanced oxidation processes (AOP, s) and comparison between photo activity of both films reveal that, indium tin oxide can be used as a suitable alternative to TiO_2 thin films for water treatment. ITO and TiO_2 thin films prepared by e-beam evaporation technique and UV light. The thin films were characterized by XRD, AFM, and UV-vis. The photocatalytic activity of ITO thin films at 500˚C is obviously higher than those of TiO_2 thin films (*Mohammad H. H. et. al., 2006*).

Mohammad H. H.,and Nasrin T.(2007),"Photocatalytic degradation of an azo dye X6G in water: A comparative study using nanostructured indium tin oxide and titanium oxide thin films", Dyes and Pigments ,**73**, 186-194. *Joshi P et. al., 2001* carried out the photocatalytic degradation of three reactive dyes, namely, Reactive Red 141 (RR141), Reactive Orange 16 (RO16) and Reactive Violet 13 (RV13). The UV illuminated TiO_2 containing aqueous suspensions found to remove color as well as chemical oxygen demand (COD). The photodegradation efficiency of these three reactive dyes was found in the order of RR141 > RO16 > RV13. These results suggest that TiO_2/UV photocatalysis may be envisaged as a method for treatment of diluted colored wastewaters not only for decolorization, but also for polishing of the COD parameter. *Hu. C. et. al., 1999* have been investigated 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. Methyl Orange using TiO_2 suspensions irradiated with a medium pressure mercury lamp. The color removal of dyes solution and dyeing wastewater reached to above 90% within 20-30 min. of photo catalytic 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.

Krishnan R. et. al., 2001 studied were carried out on methylene blue (MB) as model substrates, they discussed three aspects of TiO_2-based heterogeneous photocatalysis. We show first that a given TiO_2 sample may not be simultaneously optimal for photocatalytically driving the reduction of MB. We further show that a TiO_2 sample that strongly adsorbs either of these substrates in the dark is not optimal as a photocatalyst. The other two aspects concern circumventing the rather poor surface catalytic properties and visible light photo response of TiO_2, respectively. Strategies revolving around the visible light photo excitation of the substrate itself and metal-modification of the TiO_2 surface are described as possible solutions.

The sunlight mediated photocatalytic degradation of Rhodamine B (RB) dye was studied using hydro thermally prepared ZnO (T = 150˚C and P = 20–30 bars). Zinc chloride was used as the starting material along with sodium hydroxide as a solvent in the hydrothermal synthesis of ZnO. The effect of various parameters such as initial dye concentration, catalyst loading, pH of the medium, temperature of the dye solution, on the photodegradation of RB were investigated. The reduction in the chemical oxygen demand (COD) of the treated effluent revealed a complete destruction of the organic molecules along with color removal (*K. Bryappa et.al., 2006*).

The degradation of X6G (C.I. Reactive Yellow 2), commonly used as textile dye, can be photocatalyzed by ITO and TiO_2 thin films. The degradation can be completed in the order of minutes at optimal operational parameters. Using advanced oxidation processes (AOP,s) and comparison between photo activity of both films reveal that, indium tin oxide can be used as a suitable alternative to TiO_2 thin films for water treatment. ITO and TiO_2 thin films prepared by e-beam evaporation technique and UV light. The thin films were characterized by XRD, AFM, and UV-vis. The photocatalytic activity of ITO thin films at 500˙C is obviously higher than those of TiO_2 thin films (*Mohammad H. H. et. al., 2006*).

A comparative study between the sonolytic, photocatalytic and sonophotocatalytic oxidation processes of aqueous solutions of malachite green was carried out in the presence of carbon tetrachloride, under a low power ultrasonic field (<15 W) and using titanium dioxide as a photocatalyst. The effect of a number of parameters such as ultrasonic intensity, TiO_2 crystalline structure and the presence of CCl_4 were studied using an inexpensive reactor. Enhanced rates of sonolytic degradation of malachite green in the presence of CCl_4 were demonstrated rather than of sonolysis and photo catalysis in the presence of CCl_4 does not improve the degradation rate of malachite green in comparison with the one obtained using only sonolysis (*Ne´stor J. Bejarano-P. et.al., 2007*).

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.

Comparelli et al., 2005 immobilized ZnO powder onto transparent substrate and comparatively examined as photocatalyst for the UV induced degradation of two azo dyes, Methyle red and Methyle Orange in water. *Hasnat et al., 2005* examined photocatalytic degradation of methylene blue, a cationic dye and Procion Red, an anionic dye in TiO_2 dispersions under visible light and discussed the extent of degradation in terms of Langmuir-Hinshewood model. The degration pathway of procion Red was found to be somewhat different from Methylene Blue.

Chin-Chaun Liu et. al., 2006 also found that positively charged TiO_2 surface adsorbed more Acid yellow 17 synthetic dye in acidic pH and more degradation was achieved. *E. Bizani et. al., 2006* investigated the degradation rate for two dye solution in acidic, neutral and alkaline pH and has reported results in acidic conditions. *S. S. Reddy and B. Kotaiah, 2005* has observed the similar effect of pH on the degradation of the simulated dyeing plant effluent. *M.A. Hasnat et al., 2005* has examined Procion Red (an anionic dye) degradation under pH variation and found best results at pH 3.22

C. G. Silva et. al., 2006 has reported that degree of decolorization increases with the increasing amount of catalyst concentration up to a certain limit and beyond after that further increase in catalyst dose decolorization has been decreased. *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.

M. Muruganandham et. al., 2006; M.A.Behnajady et. al., 2005 investigated the effect of UV/Solar light intensity on the decolorization of Reactive Yellow 14 and acid yellow 23 at different light intensity. They have reported that percentage decolorization increase with increases in intensity of UV/Solar light.

M. Faisal et. al., 2005 studied the aqueous suspensions of TiO_2 containing dye derivatives acridine orange and ethidium bromide to solar radiation. It was found that the degradation of the model compounds proceeds much more rapidly in the presence of UV light source as compared to sunlight. *M. Muruganandham et. al., 2006* studied the Solar/TiO_2 process for photo catalytic decolorization of Reactive Yellow 14 dye which was completely decolorized in 80 min. *W.S. Kuo et. al., 2006* identified the application of TiO_2 film to solar photocatalysis of organic dyes, including methylene blue, RR195 and RY145. It was found that after 6-h solar irradiation, in case of TiO_2 film the degradation capability of solar photocatalytic system was significantly improved without TiO_2 film.

M. Faisal et. al., 2005; M. Muruganandham et. al., 2006; W.S. Kuo et. al., 2006 have studied the aqueous suspensions of TiO_2 containing dye derivatives to solar radiation. It was found that the degradation of the model compounds proceeds more rapidly in the presence of UV/TiO_2 light source as compared to Solar/TiO_2.

S. S. Reddy et. al., 2005 have studied the initial concentration of H_2O_2 for the reactive dye bath in the term of rate of decolorization. At 1500 mg/l concentration color removal efficiency was 99 % and further increase in dosages of H_2O_2 did not increase the color removal efficiency. *M. Faisal et. al., 2005* has studied the effect of electron acceptors such as hydrogen peroxide on the photocatalytic degradation.

Chapter 4

MATERIALS AND METHODS

This chapter describes the materials and methods used during this research, including the chemicals, glassware instrument like the, pH adjustment and analysis by UV-Vis Spectrophotometer, and procedures used to treat the dye with the Solar/TiO_2,Solar/ZnO catalysis and Solar/TiO_2/H_2O_2 and Solar/ZnO/H_2O_2. The compilation of the varying pH of solution, TiO_2 and ZnO dosages and the varying Solar contact times for the Procion Blue dyes with varying concentrations make up the experimental matrix.

4.1 MATERIALS

4.1.1 Dye

Procion Blue Herd (PBH) which is commonly used for dyeing cotton, viscose, flex and jute but is not suitable for silk, wool and polyester. Among azo dyes, those with the triazine group are particularly important due to the well-known resistance of the s-triazine to lightinduced fading Procion Blue (PB) dye sample was collected from textile industry, which is a toxic chemical having high COD value and color. The dye cannot be degraded by conventional biological treatment processes. Toxicity is the main problem encountered during biological degradation of dyes, which make it difficult to treat by biological processes. No solar photocatalytic degradation study on PBH in aqueous solution or industrial effluents containing PBH has been reported. Keeping in view, PBH usage in industries and thereby its release in the effluents, the solar photocatalytic degradation of commercial reactive dye has been investigated using different semiconductors titanium dioxide (TiO_2) and zinc oxide (ZnO).Dye sample (Procion blue) was collected from textile industries which are being used as basic coloring agent in the industry. Dye was used without further purification. Full scan of dye was taken with the help of UV-vis spectrophotometer and maximum absorbance was observed at 226nm, 276nm and 608nm. Molecular structure of Procion blue dye is illustrated in Fig-4.1.1. This dye is a toxic chemical primarily used as a dye. It is a blue powder, very soluble in water. Dye solution was prepared with the help of single distilled water.

Structure of dye

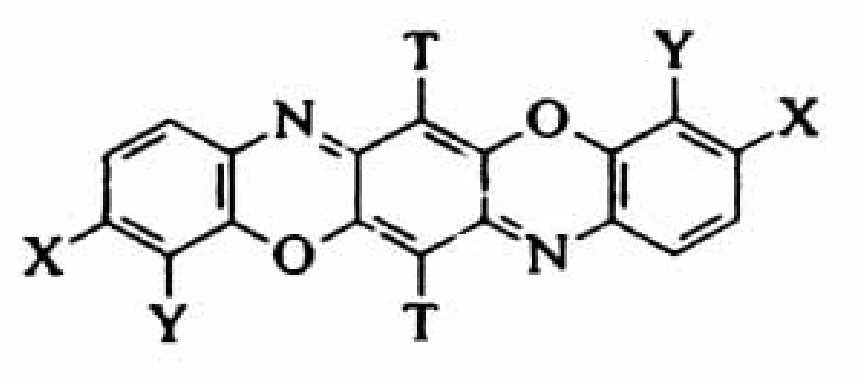


Fig- 4.1 Structure of Procion blue dye

4.1.2 Reagents and Chemicals Used

The photocatalyst TiO_2 and ZnO were used. Hydrogen peroxide was used as an oxidant.. For all the experiments single distilled water were used. Different normality of (0.1, 1M) HCl and NaOH were used for adjustment of pH of dye solution.

4.2 INSTRUMENT USED

4.2.1 pH meter

A pH meter is an electronic instrument used for measuring the pH (acidity or alkalinity) of a liquid (though special probes are sometimes used to measure the pH of semi-solid substances). A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading. 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 and HCl. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

Fig-4.2 pH meter

4.2.2 Magnetic Stirrer

It is a laboratory device that employs a rotating magnetic field to cause a stir bar (also called "flea") immersed in a liquid to spin very quickly, thus stirring it. The rotating field may be created either by a rotating magnet or a set of stationary electromagnets, placed beneath the vessel with the liquid. Magnetic stirrer was used during experimentation to solve the problem of mixing and keeping zinc oxide and titanium dioxide in suspension.

4.2.3 Air sparger

Air is continuously supplied during experiments in solar experiments in order to oxidize the organic matter.

4.2.4 Filtration

After solar photocatalytic treatment, dye was filtered through syringe filters having milipore filters of 0.45 um pore size.

4.2.5 Reaction vessel

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

Fig-4.3 Glass bowl reactor with magnetic stirrer at lab scale

4.2.6 Spectrophotometer

The spectrum was taken with UV-vis. Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer). The decolourization/degradation studies were conducted by measuring absorbance in UV/VIS spectrophotometer, having a wavelength range from 190-1100nm using a 1 cm quartz cell. All the experiments reported were carried out in a 4 ml quartz couvette. The scan speed is 200 nm/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 0-40^{o}C

Fig-4.4 uv-vis spectrophotometer

4.3 METHODS

4.3.1 Collection and storage dye sample: Dye sample was a collected from the industry which is basically used in the dyeing processes and stored in dry place protected from moisture.

4.3.2. Preparation of solution

a) **Dye solutions:** The dye solutions were prepared by adding a known amount of dye into a small amount of deionized 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 dye solutions. For most of the experiments, dye solutions of 25ppm(25mg/L) concentration were prepared by dissolving 0.025g in single distilled water and make the solution quantity to1 L. (If 1 g is present in 1 L then solution is said to be 1000 ppm and 0.1 g in 1000 ml then it becomes 100 ppm.)

b) **Hydrogen Peroxide:** Hydrogen peroxide (30% w/v) was obtained from S.D. fine-chem. Limited having M.W. of 34.01. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg (0.1 to 0.5 M oxidant dose was used in experiment).

c) **Handling and Storage of Dye**

Precautions:

Keep locked up. Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk; evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 25°C (77°F).

4.4 Analysis for decolouration/degradation

Full scan using UV-Vis spectrophotometer was taken after the treatment for the PBH dye. Solar photocatalytic treatment was done for PBH dye. The dyes was treated using ZnO and TiO_2 and the various parameters like pH, catalyst dose, concentration of oxidant, initial concentration of dye were varied and optimized.

4.5 Degradation of dye

Procion blue dye solution 25 mg/L was prepared by the single distilled water. 200 ml of sample taken in reaction vessel (1000ml capacity) and reaction vessel was covered with transparent thin foil; air is also supplied by the aerator during experimentation.

Chapter 5

RESULTS AND DISCUSSION

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

5.1 DEGRADATION OF PROCION BLUE HERD (PBH) DYE

The objective was solar photocatalytic treatment for degradation and decolourization of PBH dye using ZnO and TiO_2. The efficacy of solar photo catalytic treatment was dependent on the initial color intensity of the test solution, solar exposure time and catalyst as well as oxidant dose.

5.2 UV –Vis Spectra of PB Dye

The solar photocatalytic experiments were conducted under solar light. The decolourization and degradation was recorded in term of change in intensity of characteristics peaks. Procion Blue dye (25ppm) shows the absorption peaks at 276 and 608 nm. Fig. 5.1 shows the UV-Vis Spectra of 25 ppm i.e 25mg/L of PB dye solution. The rate of degradation was recorded with respect to change in intensity of absorption of peaks at 276 nm and rate of decolourization at 608 nm.

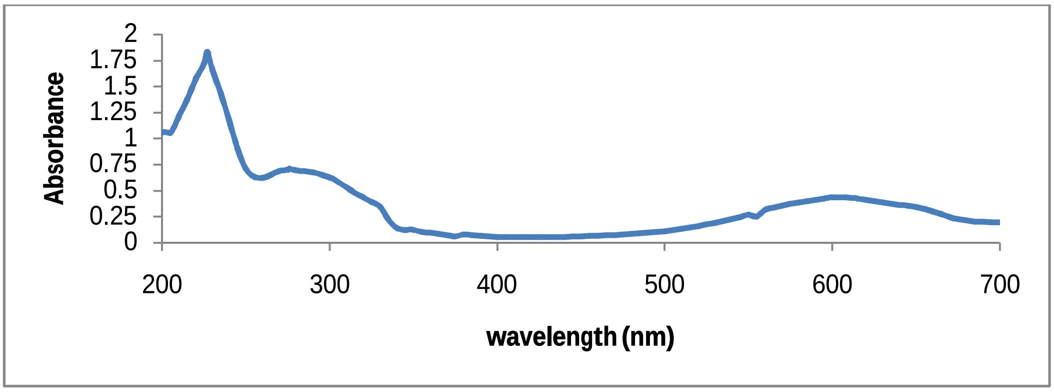


Fig- 5.1 Full scanning spectrum of PBH dye

5.3 Photolysis and Photocatalytic degradation of PBH dye

Decolourization of PBH was investigated under five different experimental conditions through solar light alone, solar/TiO_2, solar/ZnO, Dark/TiO_2, and Dark/ZnO.Fig.5.2 depicts the photocatalytic degradation of PBH under these experimental conditions. The degradation rate was recorded in terms of change in intensity of characteristic peak at 276 nm. Initially blank experiments were performed under solar irradiation without addition of any catalyst (solar alone) and only 5.61% degradation was observed.However, 21.06% and 29.63% degradation rate was achieved with Dark/TiO_2, and Dark/ZnO respectively. Then solar photocatalytic experiments were carried out using both catalysts at fixed dye concentration (25 mg/L) and catalyst loading of 0.375 (ZnO) and 0.5(TiO_2) g/L. When experiments were performed under solar irradiation with ZnO as photocatalyst (solar/ZnO), the degradation of dye was (97.89%) achieved in 75 min, whereas with TiO_2 as a photocatalyst (solar+TiO_2) only 83 % degradation of PBH was observed in the same duration. It indicates that ZnO exhibits higher photocatalytic activity than TiO_2 for the degradation of PBH.

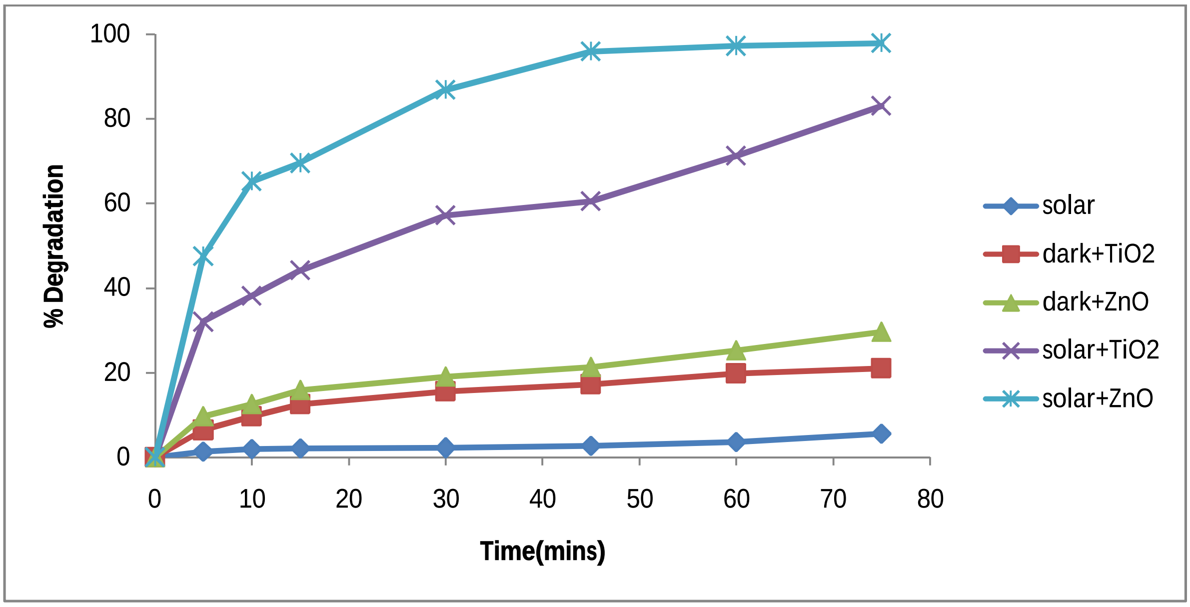


Fig-5.2 Photocatalytic degradation of PBH dye (initial dye conc. =25 mg/L,TiO_2=0.5g/L and ZnO=0.375g/L

5.4 Effect of Catalyst Dose

The catalyst dose is very important parameter which has strong influence on the degradation kinetics of dye solution. ZnO and TiO_2 catalyst were 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 catalyst varying from 0.25 to 0.625 g/L. The graphs plotted below between amount of catalyst used and percentage degradation reveals that with an increase in catalyst dose decolourization as well as degradation efficiency increases up to 0.5 g/L catalyst dose in case of TiO_2(Fig 5.3(a) and 5.4(a)) and degradation efficiency was maximum with 0.375 g/L of ZnO (Fig5.3(b) and 5.4(b).

Thus, with the increase of catalyst dosage, total active surface area increases, hence, the availability of more active sites on catalyst surface. It has also been reported that the catalyst amount has both positive and negative impacts on the photodecomposition rate. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of solar light and hence photoactivated volume of suspension decreases. Therefore the catalyst doses 0.5 (TiO_2) and 0.375 (ZnO) g/L were fixed for degradation as well as for decolourisation of PBH dye

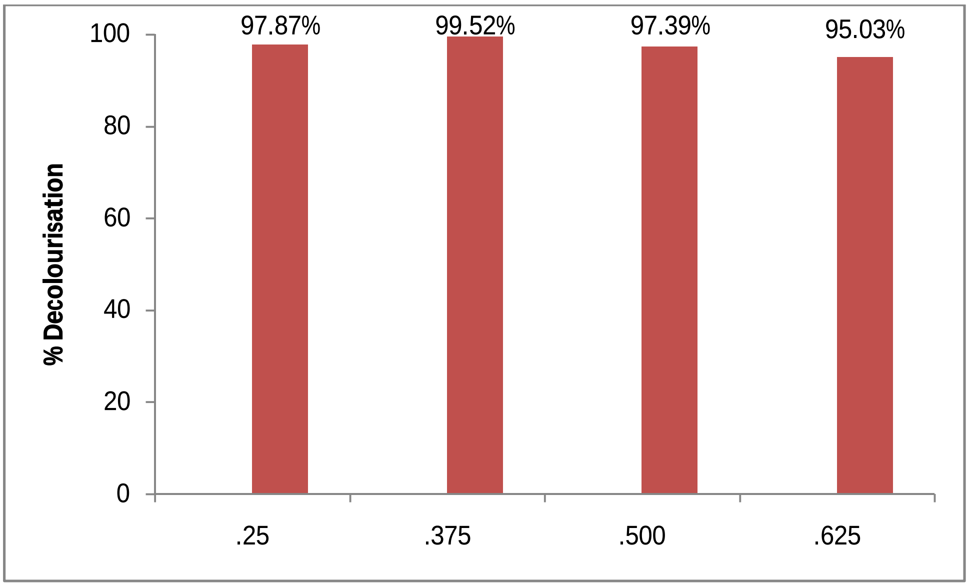


Fig-5.3(a) Effect of ZnO dose on decolourization efficiency (%) of PBH dye.

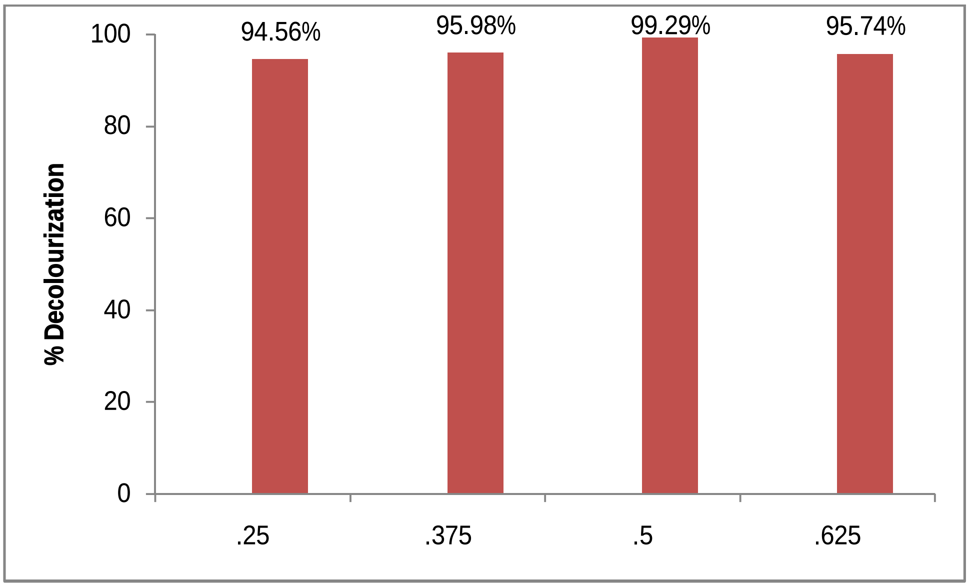


Fig-5.3(b) Effect of TiO_2 dose on decolourization efficiency (%) of PBH dye.

However degradation was 97.9% with ZnO and 83% in case of TiO_2. Irradiation time was 75 min for degradation and 60 min for decolourization.

So 0.375g/L in case of ZnO and 0.5g/L for TiO_2 was considered as the optimum dose for the degradation of procion blue dye solution (25 ppm) for subsequent analysis.

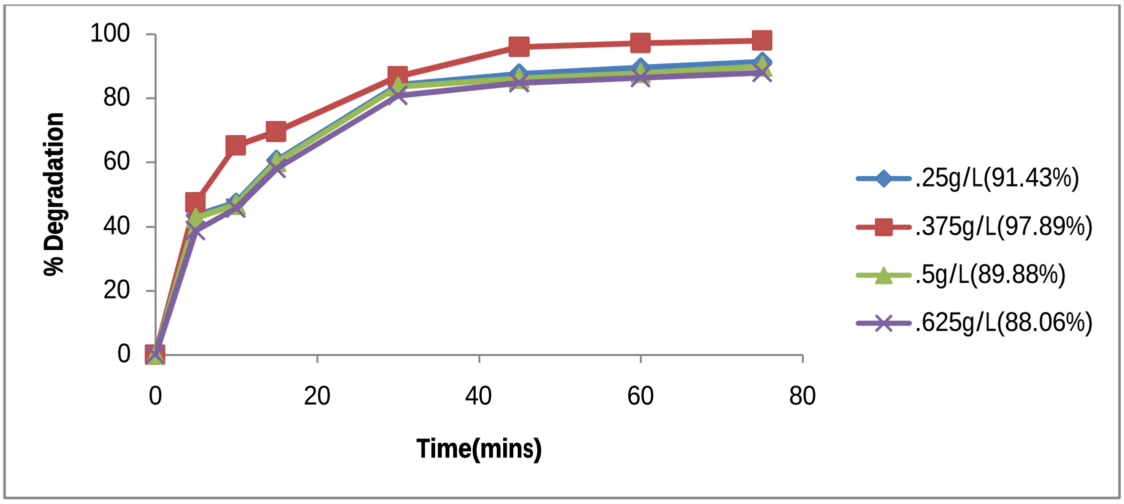


Fig-5.4(a) Effect of ZnO dose on degradation efficiency (%) of PBH dye.

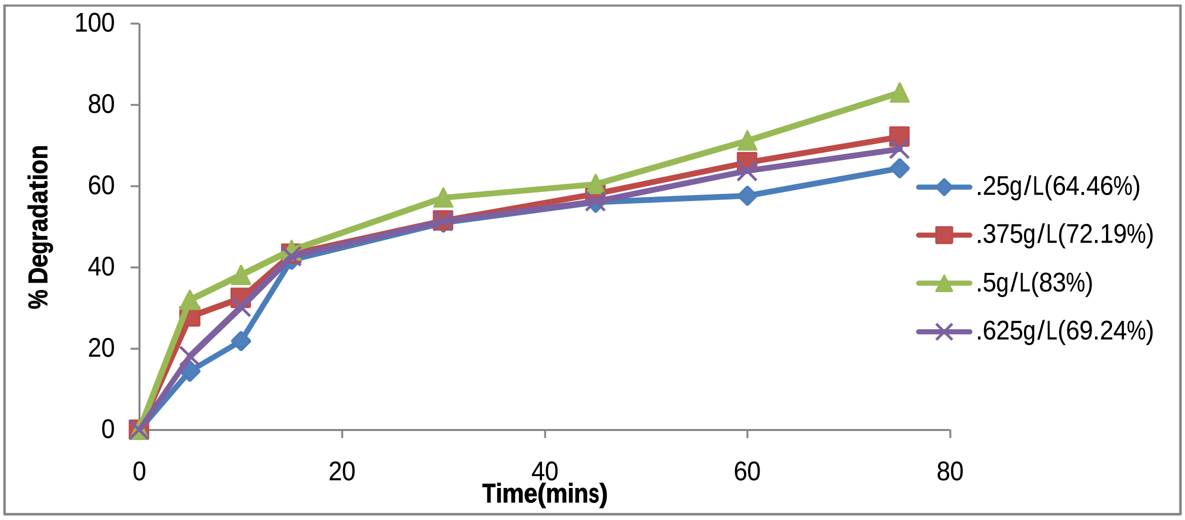


Fig-5.4(b) Effect of TiO_2 dose on degradation efficiency (%) of PBH dye

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5.5 Influence of pH

Wastewater–containing dyes is discharged at different pH, therefore it is important to study the effect of pH on decolouration of dye. In the present study, the effect of pH of the solution on the percentage photodegradation was examined in the range 2-12. Fig. 5.5(a) and 5.5(b) shows the color removal efficiency of photocatalysts as a function of pH. The results reveal that the lesser degradation of dye occurs in basic solution and higher in acidic region with TiO_2.However in the case of ZnO, the maximum degradation occurs at pH 8.The interpretation of pH factor on the efficiency of Photocatalytic degradation process can be explained on the basis of acid base property of metal oxide surface and the ionization state of ionizable organic molecule.

$$\text{M OH} + H^+ \longrightarrow MOH_2^+ (pH \leq pzc) \qquad (1)$$

$$\text{M OH} \longrightarrow MO^- + H^+ \ (pH \geq pzc) \qquad (2)$$

TiO_2 surface is positively charged in acidic media whereas it is negatively charged under alkaline condition. ZnO surface is positively charged below pH 9 based on their pzc. PBH is a anionic dye in aqueous solution. Percentage decolourization and degradation dye at various pH values are illustrated in Fig 5.5(a), 5.5(b), 5.6(a), 5.6(b). For TiO_2, the rate of decolourization and degradation increased with a decrease in pH, exhibiting maximum efficiency at pH 4.In case of ZnO optimum pH was 8.

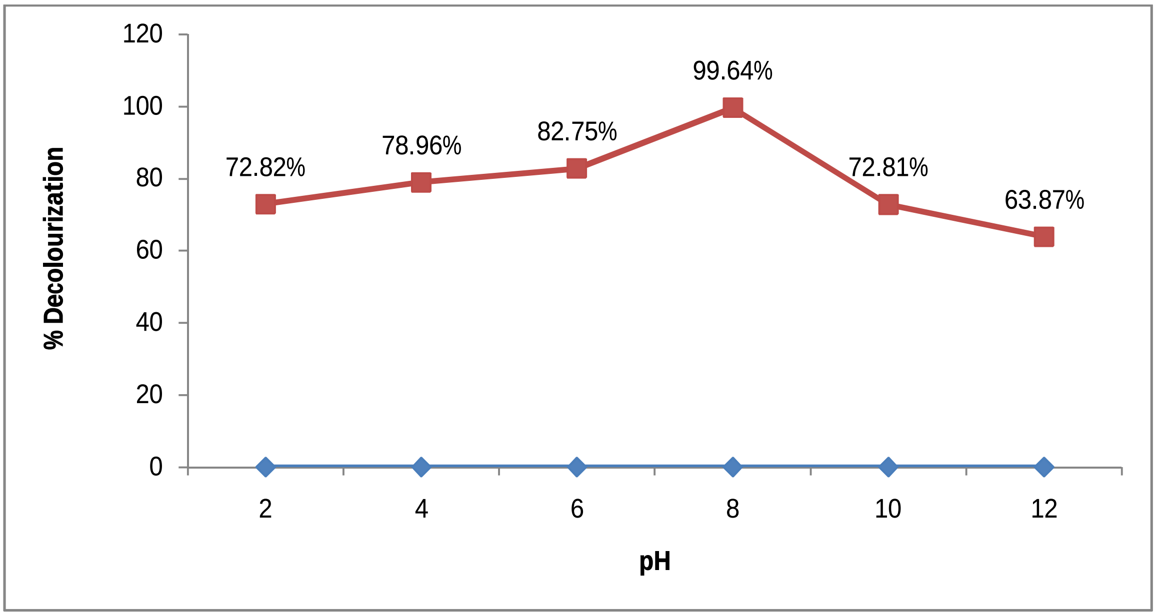

Fig-5.5(a) Effect of pH on decolourization efficiency (%) of PBH dye with ZnO (0.375g/L)

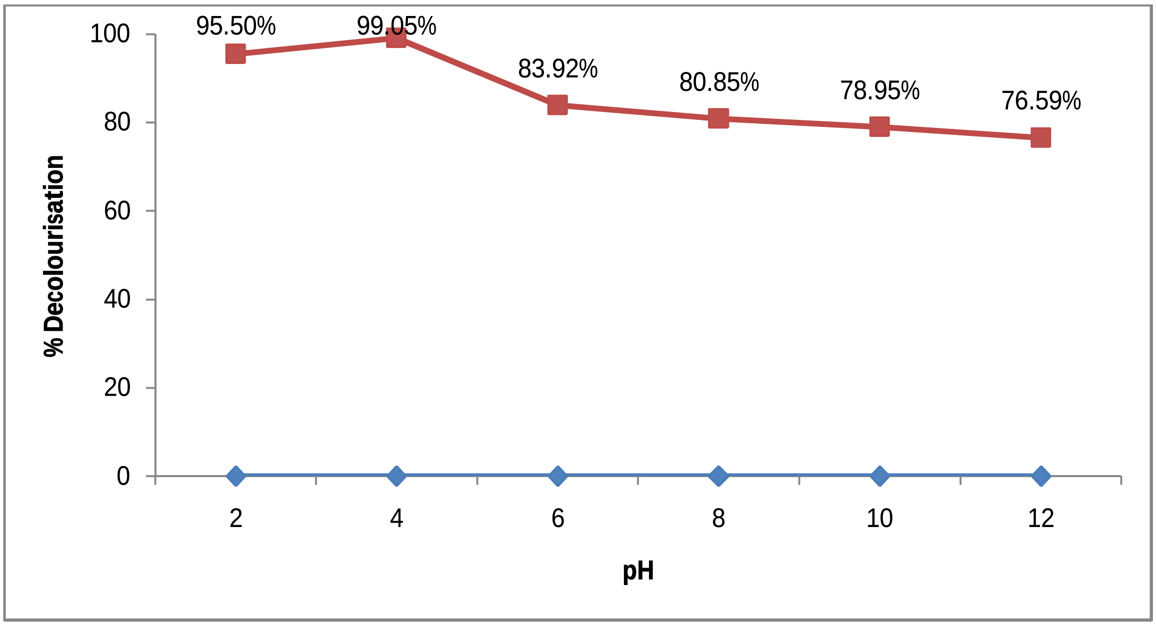

Fig-5.5(b) Effect of pH on decolourization efficiency (%) of PBH dye with TiO_2 (0.5g/L)

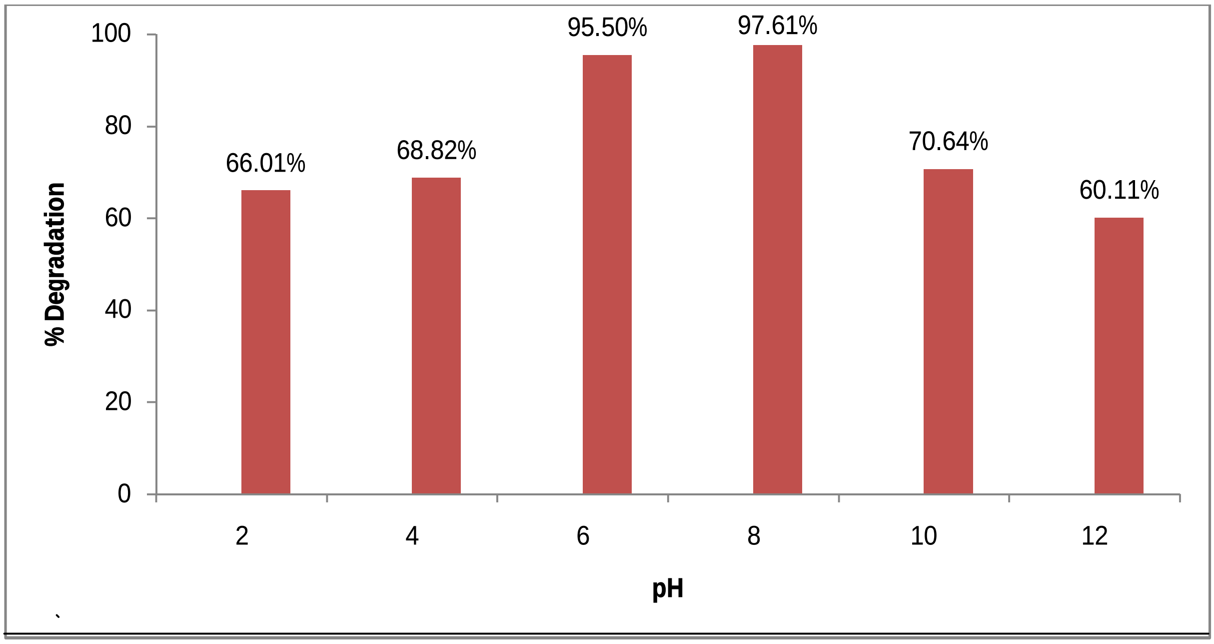

Fig-5.6(a) Effect of pH on degradation efficiency (%) of PBH dye with ZnO (0.375g/L)

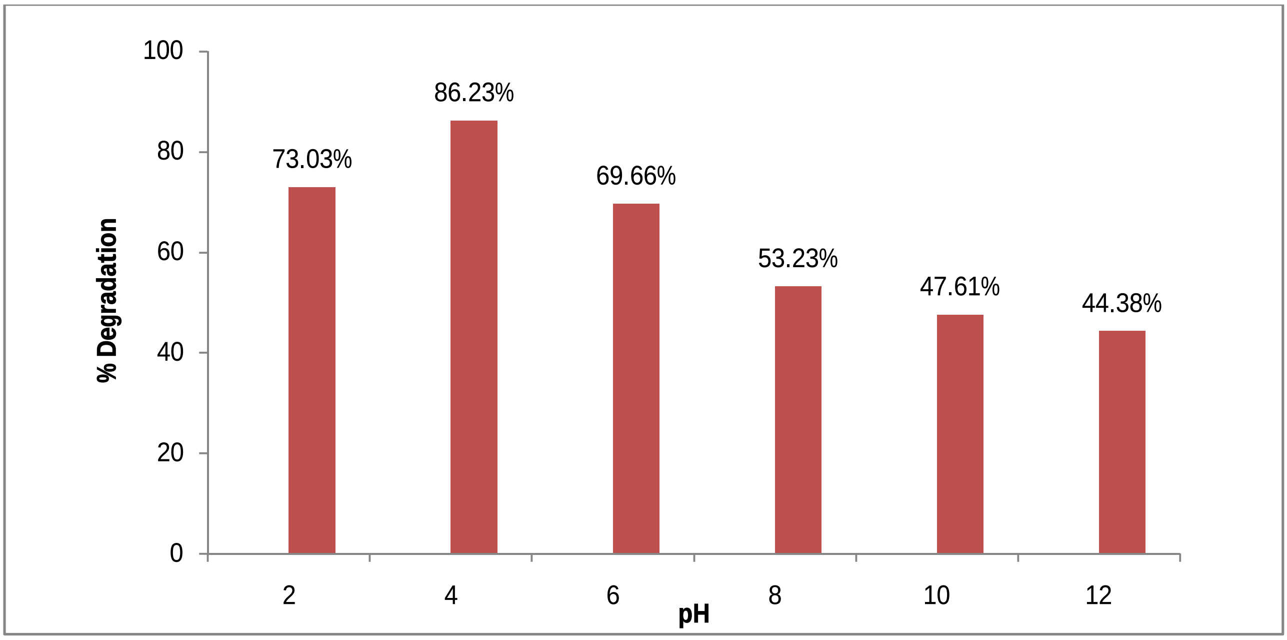

Fig-5.6(b) Effect of pH on degradation efficiency (%) of PBH dye with TiO_2 (0.5g/L)

5.6 Effect of Oxidant Dose

The rate of photocatalytic degradation of organic compounds is significantly improved by the addition of hydrogen peroxide. The oxidative photocatalytic degradation has been investigated using 25 ppm PB dye solution, at pH 4.0, catalyst dose of 500 mg/l and varying the dose of H_2O_2 dose from 0.1 to 0.5 M.Fig5.7(a) 5.7(b) shows that decolourization efficiency (%) of PBH dye with ZnO and TiO_2 as a function of H_2O_2.

However, maximum degradation efficiency (%) was achieved with 0.2 M in case of ZnO and 0.3M in TiO_2.

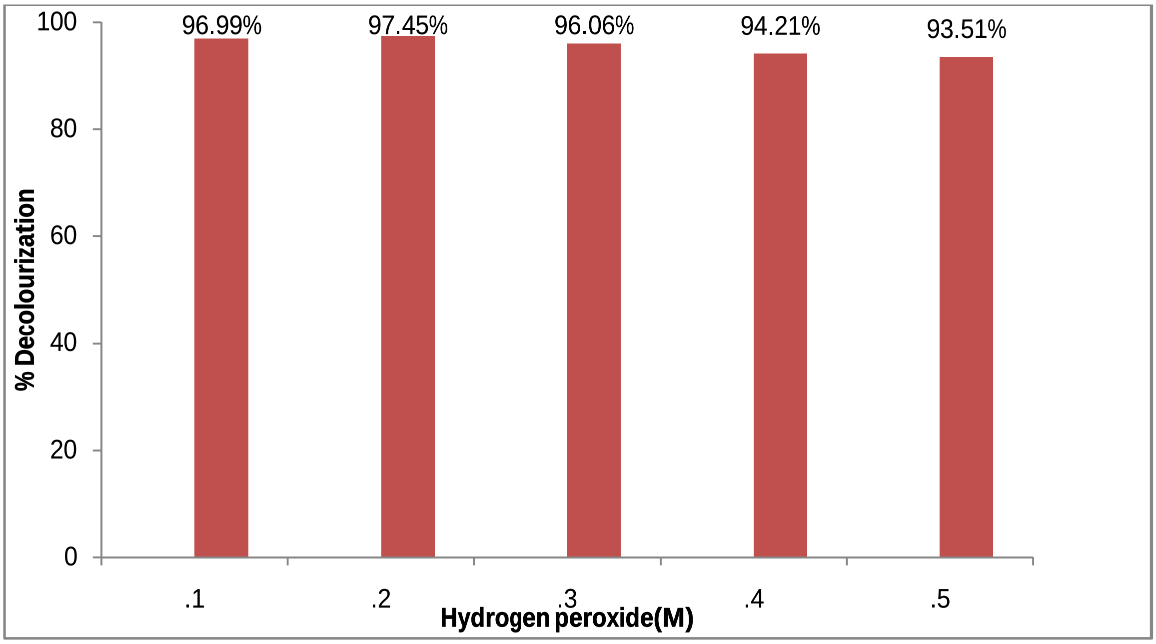

Fig-5.7(a) Effect of H_2O_2 on decolourization efficiency (%) of PBH dye with ZnO (0.375g/L) and pH=8

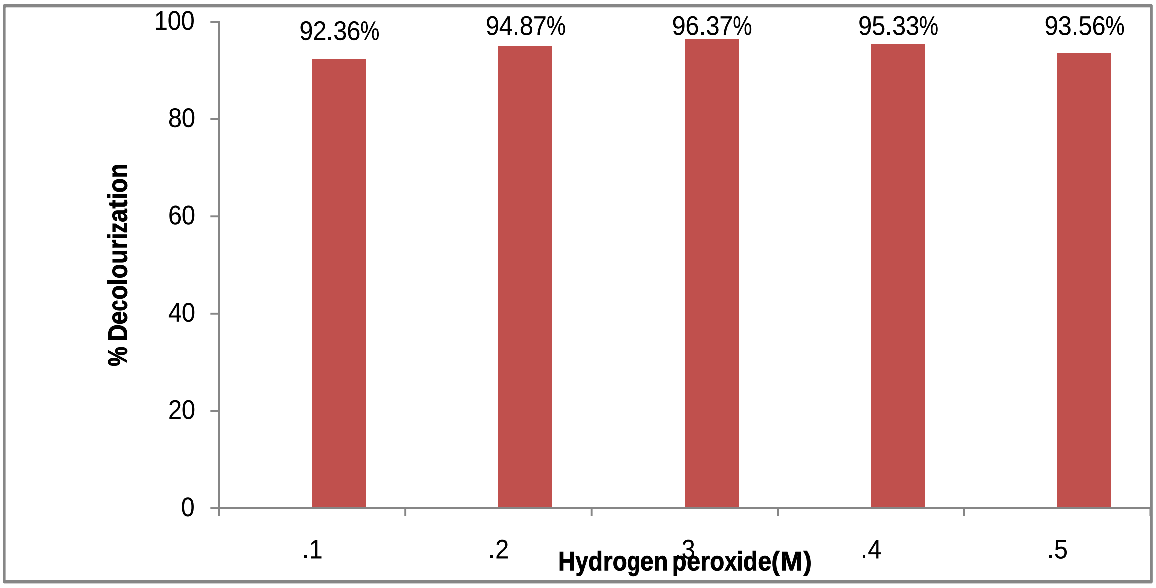

Fig-5.7(B) Effect of H_2O_2 on decolourization efficiency (%) of PBH dye with TiO_2 (0.5g/L) and pH=4

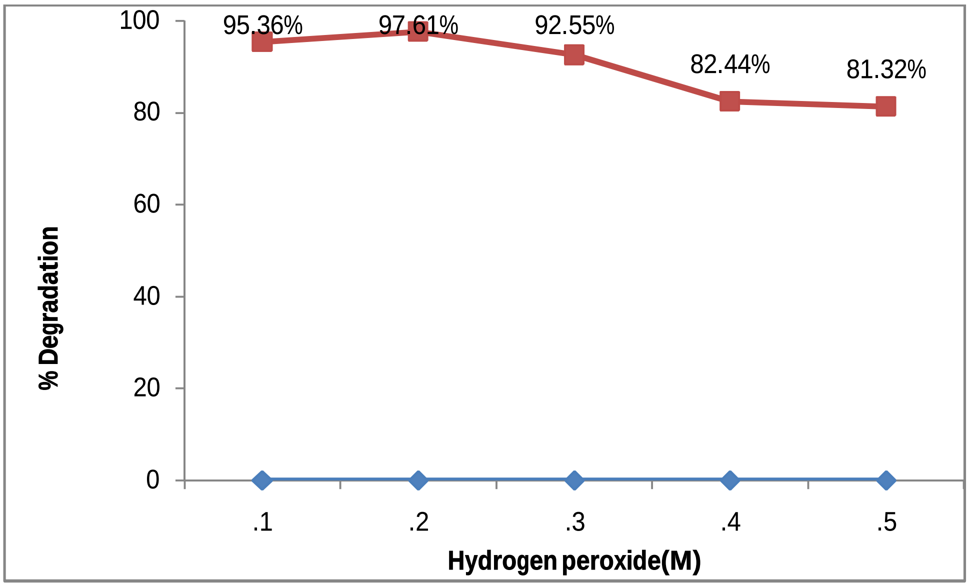

Fig-5.8(a) Effect of H_2O_2 on degradation efficiency (%) of PBH dye with ZnO (0.375g/L) and pH=8

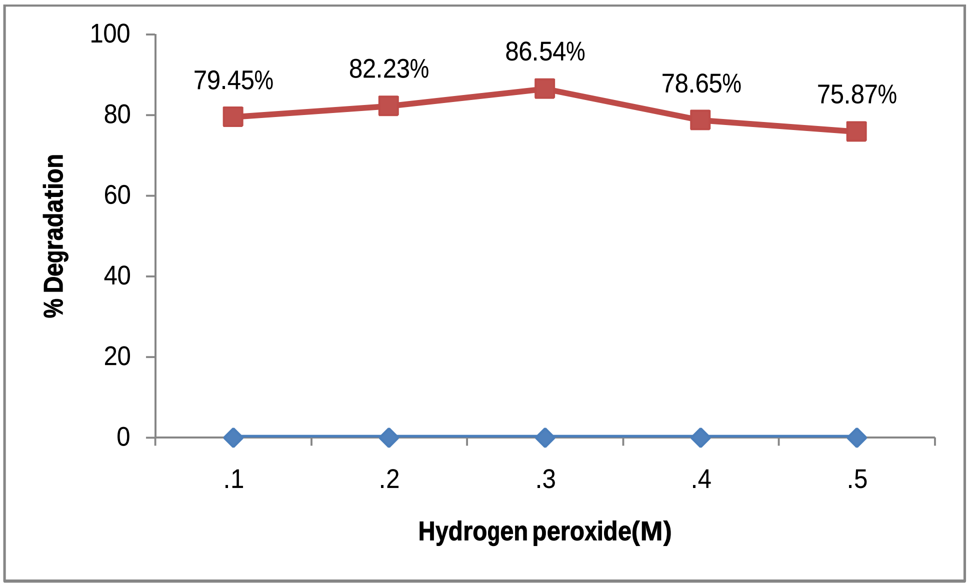

Fig-5.8(b) Effect of H_2O_2 on degradation efficiency (%) of PBH dye with TiO_2 (0.5g/L) and pH=4

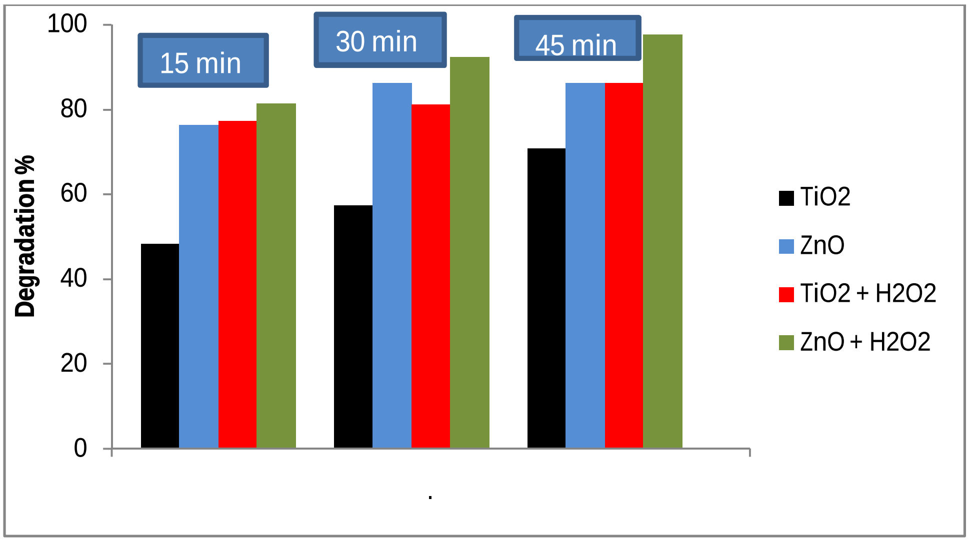

Fig-5.9 shows time dependent degradation of PBH dye using TiO_2 (0.5g/L and pH 4), ZnO (0.375g/L and pH 8), TiO2+H_2O_2 (0.5g/L, pH 4 and H_2O_2 =0.3M), ZnO (0.375g/L, pH 8 and H_2O_2=0.2M)

5.7 Effect of the Initial Dye Concentration

The pollutant concentration is very important parameter in wastewater treatment. After optimizing the experimental conditions, the Photocatalytic discoloration of PBH was carried out by varying the initial concentrations of the dye from 10 to 100 ppm. As the concentration of the dye is increased, the rate of photodegradation decreases indicating either to increase the catalyst dose or time span has to be increased for the complete removal. Fig5.10 (b) and 5.10(a) clearly shows that with increase in initial concentration of dye percentage decolourization of PBH decreases with TiO_2 as well as ZnO respectively. However percentage degradation for different concentration of dye solution is more with ZnO as compared to TiO_2 (Fig 5.11(a) and 5.11(b). 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. The increases in the dye concentration also decrease the path length of photon entering into the dye solution. At high dye concentration a significant amount of solar light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency.

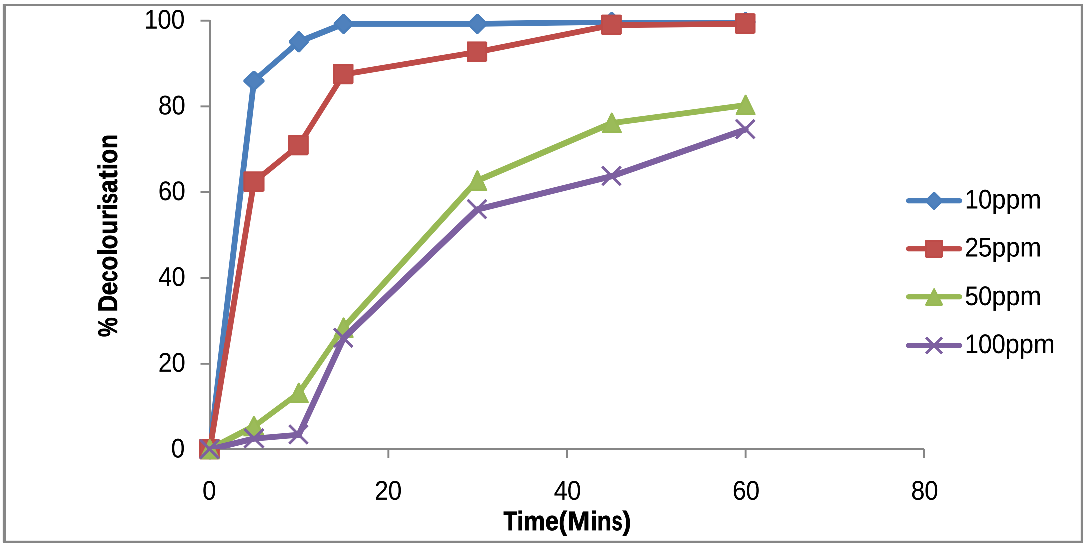

Fig-5.10(a) Effect of the initial dye concentration on photocatalytic decolourization at pH 8 & [ZnO] = 0.375 g/L

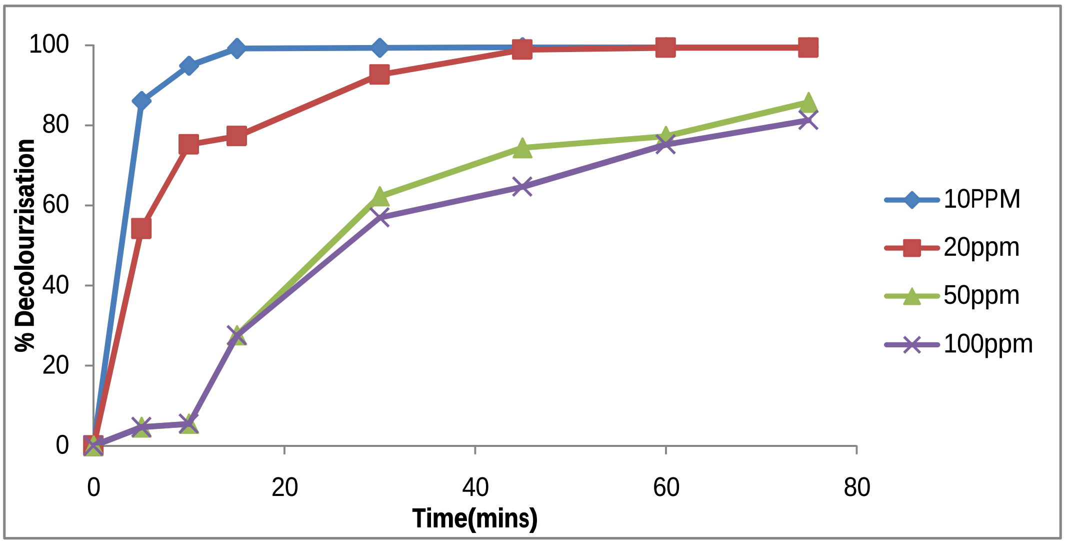

Fig- 5.10(b) Effect of the initial dye concentration on photocatalytic decolourization at pH 4 & [TiO_2] = 0.5 g/L

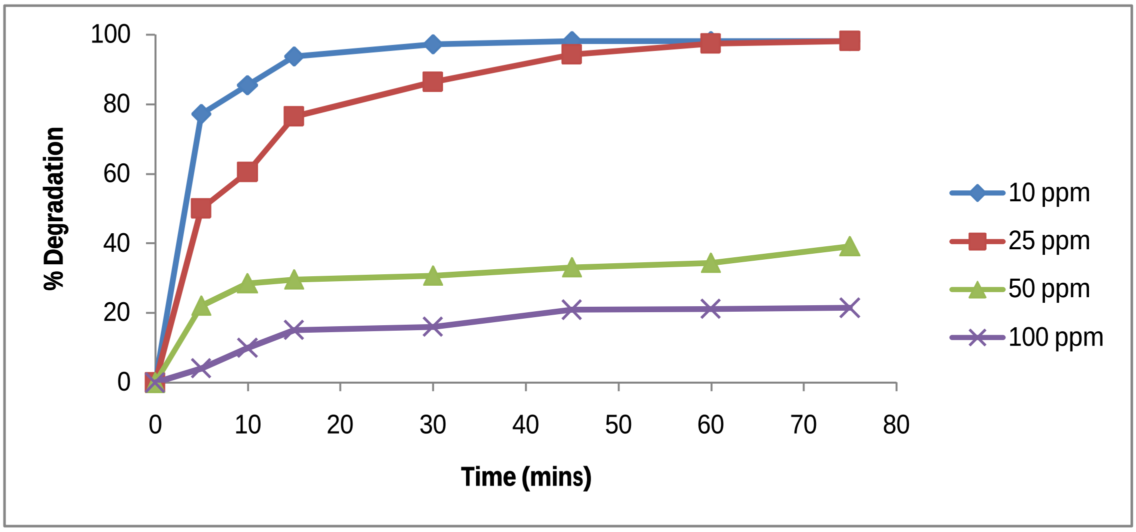

Fig- 5.11(a) Effect of the initial dye concentration on photocatalytic degradation at pH 8 & [ZnO] = 0.375 g/L

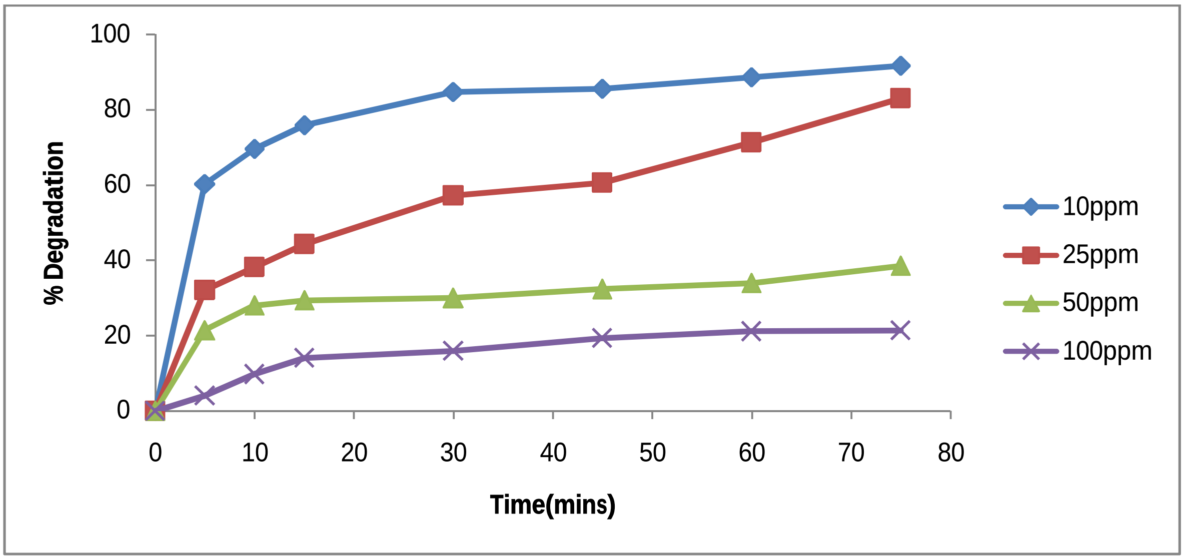

Fig- 5.11(b) Effect of the initial dye concentration on photocatalytic degradation at pH 4 & [TiO_2] = 0.5 g/L

5.8 Effect of light source

Decolourization and degradation of PBH was investigated under solar and u.v. under different conditions solar/TiO_2, UV/TiO_2, solar/ZnO and UV/ZnO. Fig 5.12(a) and 5.12(b) depict the photocatalytic decolourization and degradation of PBH under these experimental conditions.However decolourization was approx 99% under all other conditions. Talking about degradation efficiency%, it was max. in U.V./ZnO (98.17%)>solar/ZnO (97.89.53%)>U.V. /TiO_2(85.53%)>solar /TiO_2(83%).

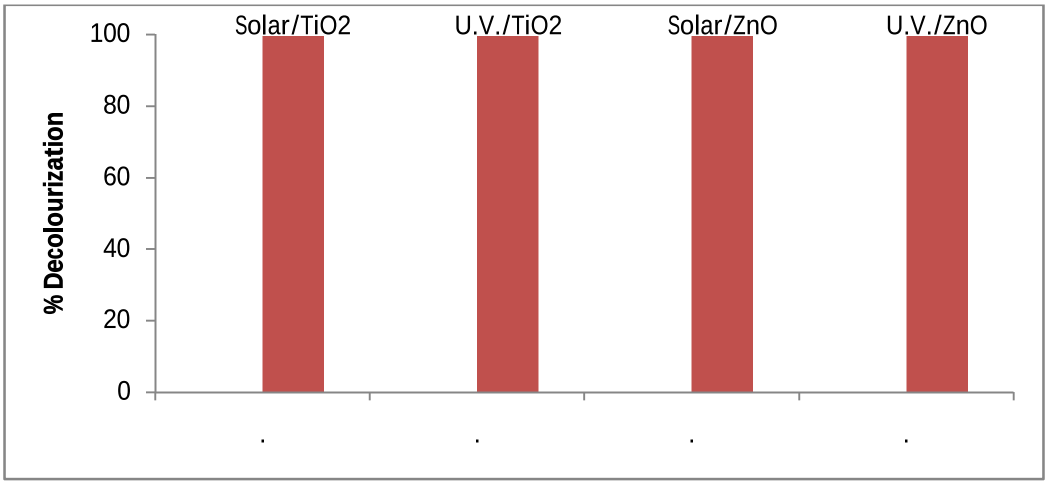

Fig -5.12(a) Effect of light source and catalyst on decolourization efficiency % on PBH dye with TiO_2 (0.5g/L) and ZnO (0.375g/L)

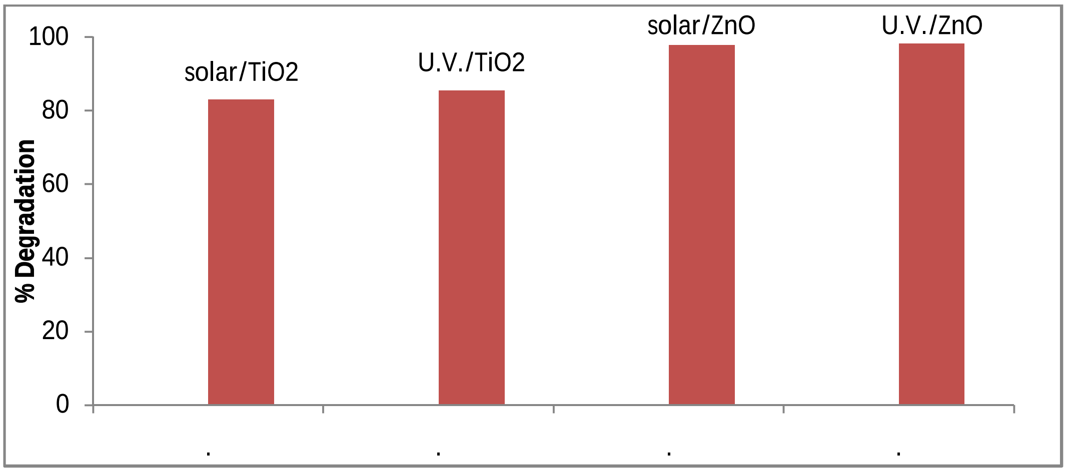

Fig -5.12(b) Effect of light source and catalyst on degradation efficiency % on PBH dye with TiO_2 (0.5g/L) and ZnO (0.375g/L)

5.9 Degradation of Dye during Course of Reaction

Fig 5.13 shows the degradation of Procion Blue dye during the reaction time. The primary absorption peaks of the original dye solution were at 276 nm and 608 nm. As the reaction proceeds, the two peaks disappeared gradually and the full scanning spectrum pattern changes obviously after 45 min. At the end of the 45 min of reaction time, there was no evident absorption peak observed. It indicates that the main chromophores in the original dye solution were destroyed with the solar photocatalytic reaction and proves that Procion Blue was fully decomposed.

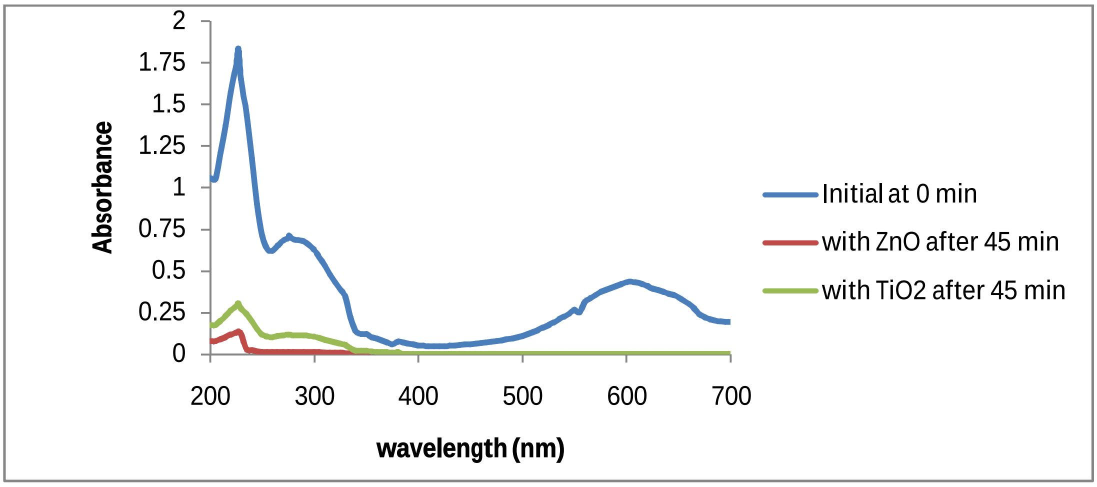

Fig- 5. 13 The full scanning spectrum of PBH (25 ppm) under optimized conditions

CONCLUSION

Wastewater containing dyes emanating from textile mills are strongly coloured and carcinogenic in nature. In order to tackle this menace of pollution problem, it is desirable to degrade the dye into non toxic form before its discharge into the main stream. They are not easily degraded by aerobic bacteria and forms toxic compounds under the action of anaerobic bacteria. Therefore, it becomes imperative to completely degrade these organic compounds before their discharge. Such pollutants cannot be completely degraded by well established techniques like coagulation, flocculation, precipitation, adsorption, membrane separation, aerobic biological treatment. The incapability of conventional wastewater treatment methods to effectively remove such pollutants leads to explore the new, efficient and cost effective treatment systems. In order to meet stringent environmental regulations, the latest development is the oxidation of these biorecalcitrant organic compounds. These radicals have high oxidizing power superior to other usual oxidants and results in complete degradation. The methods are called advanced oxidation processes (AOP's). AOP's include homogenous and heterogeneous photocatalytic processes, however the latter being more promising technique for the degradation of organic pollutants. Photocatalytic process relies on the activation of semiconductor results in the generation of electrons and holes. This hole can react with water to produce hydroxyl radical which results in series of redox reaction to destroy the pollutants.

Many studies have been reported for the use of photocatalyst in the transformation of dyes into simpler end products but the work on photocatalytic degradation of reactive dyes in literature is limited as compared to other dyes Procion Blue (PB) dye was collected from textile mill. Photo degradation of PB dye was performed in specially designed reaction vessel under direct sunlight and constant stirring of solution was ensured. The degradation of the PBH dye in water was investigated in laboratory-scale experiments, using Zno and TiO_2.Experiments were performed in slurry mode in solar light at optimized condition. The decolourization and degradation of dye has been investigated by measuring absorbance. Various process parameters like catalyst dose, pH, concentration of oxidant, initially pollutant concentration were varied and their effects have been analyzed.

The work done has been presented in five chapters. After introducing the problem and its content in the first chapter, in the second chapter there is brief discussion of treatment technologies, the study begins with the literature review on photocatalyic degradation of various dyes in the third chapter. In the fourth chapter, experimental materials and methods have been discussed in detail. Results and their discussion of solar photocataytic degradation of model dye compound have been presented in fifth chapter.

In the case of PB dye (25ppm), TiO_2 dose was optimized to be 0.5g/l, at operating pH of 4.0 along with oxidant concentration of 0.3M. In case of ZnO, parameters optimized were pH 8, catalyst dose of 0.375g/L and oxidant concentration of 0.2M. In case of PB dye 83% degradation was achieved with TiO_2 and 97 % with ZnO at optimized parameters (pH and catalyst dose) in 75 min.However with the addition of oxidant degradation time has been reduced to 45 min and degradation rate has also been increased from 83% to 86.54% in case of TiO_2.

Comparison of photocatalytic activity of catalysts has clearly indicated that the ZnO is the more efficient photocatalyst than TiO_2 for decolourization and degradation of PBH dye. Experimental results with H_2O_2 have clearly indicated of being TiO_2 more efficient in terms of % age increase in degradation without H_2O_2 in comparison to ZnO. However, degradation rate being almost same in U.V. and solar light point towards efficiency of solar light which is available free of cost. So experimental work done has indicated of being ZnO more efficient in degradation efficiency (%) under solar light as compared to TiO_2.

REFERENCES

A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, Photocatalytic A. Uygur, An overview of oxidative and photooxidative decolourization treatments of textile waste-waters, J. Soc. Dyers Colour. 113, (1997), 211–217.

A.T. More, A. Vira, S. Fogel, Biodegradation of trans-l, 2-dichloroethylene by methane utilizing bacteria in an aquifer simulator, Environ. Sci. Technol. 23 ,(1989), 403–406.

Alinsafi, F. Evenou, E.M. Abdulkarim, M.N. P. Zahraa, A. Benhammou, A. Yaacoubi and A. Nejmeddine, “Treatment of textile industry wastewater by supported photo catalysis”, Dyes and Pigments,74, (2007),439-445.

Bianco-Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano, Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO_2 suspensions, Environ. Sci. Technol. 35 (2001), 971–976.

C. Galindo, P. Jacques, A. Kalt, Photochemical and photocatalytic degradation of an C. Guillard, H. Lachheb, A. Honas, M. Ksibi, J.M. Herrmann, Influence of chemical indigoid dye: a case study of acid blue 74 (AB74), J. Photochem. Photobiol. A:Chem. 141, (2001), 47–56

C. Hu, J. C. Yu , Z. Hao, P.K. Wong, “Effects of acidity and inorganic ions on the photocatalytic degradation of different azo dyes”, Applied Catalysis B: Environmental, 46, (2003), 35–47.

C.G.Silva, W.Wangand J.L.Faria, “Photocatalytic and photochemical degradation of mono-,di-,and tri-azo dyes in aqueous solution under UV irradiation”, (2006).

Carlos A.K. Gouvea, Fernando Wypych, Sandra G. Moraes, Nelson Duran, Noemi Nagata, Patricio Peralta-Zamora, Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, Chemosphere 40 (2000) 433–440.

Chin-Chuan L., Yung-Hsu H., P., C.-H. Li and C.-L. Kao, **“**Photodegradation treatment of azo dye wastewater by UV/TiO_2 process”, Dyes and Pigments , 12, (2006)**,** 191-195.

Darinka Brodnjak V. and Alenka Majcen-Le-M.,“Reactive dye decolorization using combined ultrasound/H_2O_2”, Dyes and Pigments, 59, (2003), 173–179.

G.L. Puma, A. Brucato, Dimensionless analysis of slurry photocatalytic reactors using two-flux and six-flux radiation absorption–scattering models, Catal. Today 122 (2007) 78–90.

I. A. Salem ,Mohamed S. and El-Maazawi, “Kinetics and mechanism of color removal of methylene blue with hydrogen peroxide catalyzed by some supported alumina surfaces”, Chemosphere, 41**,**(2000), 1173-1180.

I. Arslan, I.A. Balcioglu, T. Tuhkanen, D. Bahnemann, H_2O_2/UV-C and Fe/UV-C versusTiO_2 /UV-A treatment for reactive dye wastewater, J. Environ. Engg. 126 (2000) 903–911.

J. Weber, V.C. Stickney, Hydrolysis kinetics of reactive Blue 19-vinyl sulfone, Water Res. 27 (1993) 63–67.

Joshi P, Purohit J and Neti N.R, “Photocatalytic degradation of reactive dyes and simulated dye bath wastewater”, Water Sci Technol., 43, .(2001),313-320.

K Byrapa, A K Subramani, S A., K M Lokanatha R. , R Dinesh and M Yoshimur,” Photocatalytic degradation of Rhoda mine B dye using hydro thermally synthesized ZnO”, Bull. Mater. Sci**., 29**, (2006),433-438.

K.W. Scharmm, M. Hirsch, R. Twelve, O. Hutzinger, A new method for extraction of C.I. Reactive red 4 and its derivatives from water, Water Res. 23 (1988) 1043–1045.

Krishnan Rajeshwar, C. R. Chenthamarakshan, Scott G. and Miljana D., “Titania-based heterogeneous photocatalysis. materials, mechanistic issues, and implications for environmental remediation”, Pure Appl. Chem., **73**, (2001), 1849–1860.

M. Faisal M. Abu Tariq and M. Muneer, “Photocatalyzed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania”, Dyes and Pigments, (2005)**,** 1-7.

M. Muruganandham and M. Swaminathan**,** “Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO_2-UV process”, Dyes and pigment, 68, (2006) 133-142.

M. Muruganandham and M. Swaminathan,”Solar driven decolorisation of Reactive Yellow 14 by advanced oxidation processes in heterogeneous and homogeneous media”, Dyes and Pigments, (2006).

M.A. Behnajady, N.Modirshahla and R. Hamzavi ,“kinetic study on photocatalytic degradation of C.I. acid yellow 23 by ZnO photocatalysis”, Journal of hazardous material, (2005).

M.A. Hasnat, I.A. Siddiquey and A. Nuruddin, “Comparative photocatalytic studies of degradation of a cationic and an anionic dye”, Dyes and Pigments, 66 , (2005) 185-188.

M.S.T. Gonclaves, A.M.F. Oliveira-Campose, E.M.M.S. Pinto, P.M.S. Plasencia, M.J.R.

Mohammad H. H.,and Nasrin T,“Photocatalytic degradation of an azo dye X6G in water: A comparative study using nanostructured indium tin oxide and titanium oxide thin films”, Dyes and Pigments ,**73**, (2007)186-194.

N. Daneshvar, D. Solari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2 , J. Photochem. Photobiol. A: Chem. 157 (2003) 111–116

N. Stock, J. Peller, K. Vinodgopal, P.V. Kamat, Combinative sonolysis and photocatalysis

Ne´stor J. B.-P. and Marco F. S.-H. (2007), “Sonophotocatalytic degradation of congo red and methyl orange in the presence of TiO_2 as a catalyst”, Ultrasonics Sonochemistry, 14, 589–595.

Pekakis PA, Xekoukoulotakis NP and Mantzavinos D.,” Treatment of textile dye house wastewater by TiO_2 photocatalysis”, Water Res. ,40, (2006),1276-86.

R. Camp, P.E. Sturrock, The identification of the derivatives of C.I. Reactive Blue 19 in textile wastewater, Water Res. 24 (1990) 1275–1278.

R. Comparelli , E. , M.L. Curri, P. , G. Mascolo, R., and A. Agostiano , “Photocatalytic degradation of azo dyes by organic-capped anatase TiO_2 nanocrystals immobilized onto substrates”, Applied Catalysis B: Environmental ,55 , (2005),81–91.

S. S. Reddy and B. Kotaiah, “Decolorization of simulated spent reactive dye bath using solar / TiO_2 / H_2O_2”, Int. J. Environ. Sci. Tech. **2**, (2005), 245-251**.**

S.S. Patil, V.M. Shinde, Biodegradation studies of aniline and nitrobenzene in aniline plant waste water by gas chromatography, Environ. Sci. Technol. 22 (1988) 1160–1165.

W.S. Kuo and P.H. Ho,”Solar photo catalytic decolorization of dyes in solution with TiO_2 film”, Dyes and Pigments, **71**, (2006), 212-217.

Zulkarnain Z. , C., Mohd Zobir H., A. and Nor Azah Y., “Electrochemical-assisted photodegradation of dye on TiO_2 thin films: investigation on the effect of operational parameters”, Journal of Hazardous Materials, B118, (2005), 197–203