STUDIES ON THE PHOTOCATALYTIC DEGRADATION OF DYE AND TEXTILE WASTEWATER

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DECLARATION

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

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CERTIFICATE

This is to certify that the dissertation entitled, **"Studies on the photocatalytic degradation of dye and textile wastewater"**, is an authentic work carried out by Mr. Chhotu Ram student of M.Tech. (Env. Sc. & Tech.) Thapar University, Patiala, during the year 2007-2008, 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, associate ship, fellowship or any other similar title to any other university or institute.

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ABSTRACT

The release of dyes into the receiving water bodies is deleterious, not only because of their color, but also because 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. TiO_2 has been demonstrated to be excellent catalyst and its behavior is well documented in the literature.

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. Although the strong potential of photocatalytic process for wastewater treatment is widely recognized but its technical development at industrial scale is not met with much success due to its high operating cost. Taking all these facts into consideration, in the present study, Procion Blue (PB) dye and effluent was collected from textile mill. Photo degradation of PB dye was performed in specially designed reaction vessel in the photoreactor equipped with UV tubes and constant stirring of solution was ensured at constant temperature. Experiments were performed in slurry mode in both UV and solar light at optimized condition. The degradation of dye and textile effluent has been investigated in terms of change in color

by measuring absorbance, reduction in COD and solid content. 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 four chapters. After introducing the problem and its content in the first chapter, the study begins with the literature review on photocatalyic degradation of various dyes and textile effluents in the second chapter. In the third chapter, experimental materials and methods have been discussed in detail. Results and their discussion of photocataytic degradation of model dye compound and real effluent has been presented in fourth chapter.

In the case of PB dye (25ppm), TiO_2 dose was optimized to be 500 mg/l, at operating pH of 4.0 along with oxidant concentration of 300 mg/l at UV intensity of 25 W/m^2. In case of textile wastewater, parameters optimized were pH 4.0, catalyst dose of 2.5g/l and oxidant concentration of 900 mg/l. In case of PB dye 82% degradation was achieved in solar light and 89 % in UV light at the optimized parameter, While the treatment of real effluent yields COD reduction from 1250 to 340 mg/l, TDS reduction from 5770 to 2370 mg/l and color reduction from 890 PCU to 180 PCU after 4 hrs of UV treatment. In solar photocatalysis, COD was reduced from 1250 to 260, TDS from 5770 to 1920, Color from 890 PCU to 202 PCU and more than 80% degradation was achived after 5 hrs of treatment.

The results of photo degradation of dye and textile mill wastewater showed that heterogeneous photocatalytic could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater. The investigations demonstrate the importance of selecting the optimal degradation parameters for practical applications of this operation.

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CHAPTER-1

Introduction

Water is basic requirement in all industrial processes, domestic and commercial activities, so the wastewater generated from different activities contains various contaminants which are harmful for both flora and fauna existing an this planet. The industrial operations mainly pharmaceutical, textile, pesticides and other organic chemicals manufacturing industries generate waste water containing phenolic compounds and various dyes. These effluents are intensely colored and are contaminated with high concentration of organic compounds such as suspended and dissolved salts and many other recalcitrant compounds. Even small concentration of these compounds present in effluent causes toxicity and foul odors to water. If these effluents are improperly treated, they will pose a serious threat to all aquatic species because hydrolysis of the pollutants in waste water can produce a great deal of toxic products. Degradation of theses non-biodegradable organic compounds is not possible by conventional biological treatment processes, so there has been a lot of interest in application of the advanced oxidation processes (AOP's) for the removal of such organic compounds. Many processes such as photolysis, photocatalytic oxidation, ozonation, Fenton oxidation, wet air oxidation and membrane separation has been proposed for the degradation of these compounds even at low concentration (*Naresh N. Mahamuni et al., 2005; Jun Wang et al., 2005*).

1.1 THE PROBLEMATIC OF WATER CONTAMINATION

One of the characteristics that best define today's society is the production of waste products. There is practically no human activity that does not produce waste products and in addition there is a direct relationship between the standard of living in a society or country and the amount of waste products produced. Approximately 23% of the world's population live in developed countries, consume 78% of the resources and produce 82% of the waste products. In addition, it has to be pointed out that the volume of residual waste increases in an exceptional way with regards to a country's level of industrialization. At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide, and it is estimated that 1,000 new chemical substances are added to the list each year.

Large contrasts are reflected in the problems related to the rational management of water, which cannot be dealt with in a unilateral way, but by many different procedures. The countries with sustainable development have, one by one, confronted the problems related to biological contamination, with the levels of heavy metals, with the intensive use of nutrients, and with organic contaminants at very low levels. Water disinfections, the treatment of effluents before being discharged into water systems, the limitation and substitution of nitrates and phosphates in products that are used on a massive scale and the development in analytical chemistry and in ecotoxicology are examples of some of the "tools" used to combat these problems. It must be noted that the time scale to resolve each problem as it arises, is always shorter. The problems derived from the toxicological effects of organic compounds, which are active at very low levels, must be resolved at the same time as water disinfection for rural communities. It is clear that innovative procedures are needed to deal with this wide range of problems, which vary notably in its application scale and the complexity of the problems.

Relatively recently, the discharging of waste in the environment was the way of eliminating them, until the auto-purifying capacity of the environment was not sufficient. The main problem stems from waste coming from industry and agriculture, despite the fact that the population also plays an important role in environmental contamination. Phenols, pesticides, fertilizers, detergents, dyes and other chemical products are disposed of directly into the environment, without being treated, via discharging, controlled or uncontrolled and without a treatment strategy. In this general context, it is very clear that the strategy to continue in the search of solutions to this problem that every day presents a sensitive growth, mainly in the developing countries, it will be guided by two fundamental aspects:

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

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 1.1).

Table 1.1 Black lists of chemicals 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.

The presence of this type of pollutant in an aqueous dissolution is especially problematic as the residual waste cannot be stored indefinitely (as is the case with some solid waste) and it has the peculiarity that a small volume of water is able to contaminate much greater volumes of water. It must also be pointed out that a wide spectrum of compounds can transform themselves into potentially dangerous substances during the drinking water treatment process, particularly by chlorination, as is the case of the precursor compounds of the formation of chlorocarbons.

1.1.1 Textile Wastewater

In this general context of the environmental problems caused by different kinds of pollutants, wastewater coming from the textile industry has been discussed in this regard. Textile wastewater processing is one of the most important industries in the world and it employs a variety of chemicals, depending on the nature of the raw material and product. Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances. The removal of color from textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern. In addition, only 47% of 87 of dyestuff are biodegradable (*Paggaand Brown, 1986*). It has been documented that residual color is usually due to insoluble dyes which have low biodegradability (*A.A.-Kdasl et.al., 2004*).

So textile wastewaters make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition (*Venceslau et al., 1994*). If these effluents are improperly treated, they will pose bad threats to all species on the earth because of the hydrolysis of the pollutants in the wastewater can produce a great deal of toxic products (*Jun Wang et. al 2005*).

1.1.2 Textile Wastewater Characteristics

Composite textile wastewater is characterized mainly by measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dissolved solids (DS). Typical characteristics of textile industry wastewater are presented in Table 1.2. Results in Table shows a large extent of variation from plant-to-plant and sample-to sample. As presented in Table 1.2, COD and BOD values of composite wastewater are extremely high as compared to other parameters. In most cases BOD/COD ratio of the composite textile wastewater is around 0.25 that implies that the wastewater contains large amount of non-biodegradable organic matter.

Table 1.2 Composite Textile Industry Wastewater Characteristics

S. No.	Parameters	Values
1.	pH	7.0- 9.0
2.	Biochemical Oxygen Demand (mg/L)	150 – 12,000
3.	Chemical Oxygen Demand (mg/L)	80 – 6,000
4.	Total Suspended Solids (mg/L)	15 – 8,000
5.	Total Dissolved Solids (mg/L)	2,900 -3,100
6.	Chloride (mg/L)	1000 – 1600
7.	Total Kjeldahl Nitrogen (mg/L)	70 – 80
8.	Color (PCU)	50-2500

Source: (Sheng and Chi, 1993; Tzitzi et al., 1994; Venceslau et al., 1994; Cleaner Production Program-CPP, 2002; A.A.-Kdasl et.al., 2004)

1.1.3 Source of Textile Effluent

Textile production is one of the most polluting industries (*Vandevivere* et al*., 1998*). The effluent contains several types of chemicals such as dispersants, leveling agents, acids, alkalis and various dyes. Production processes not only generate heavily polluted wastewater, but also waste heat, solid waste and exhaust gas. Generally, textile mills produce mixed wastewaters in large quantities, up to 600 m^3 per kg fabric, that are characterized by high organic load, having COD of up to 1000 mg due to the presence of dyes. Large quantity of water is consumed in the washing of fabric at the end of each process thereby producing huge amount of waste water. In order to comprehend the effluent problems facing the textile industry it is necessary to be familiar with the processes which result in effluent production. Thus, composition of effluent and associated water pollutants are different at each step of processing. As seen in the Table 1.3, textile effluents are strongly colored, high in COD and BOD due to fiber residues and suspended solids (*AEPA, 1998*). They can contaminate water with oils, grease, and waxes while some may contain heavy metals such as chromium, copper, zinc and mercury (*EPA, 1974*).

Table 1.3 Effluent Characteristics from Textile Industries

Process	Effluent composition	Nature
Sizing	Starch, waxes, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), wetting agents	High in BOD, COD
Desizing	Starch, CMC, PVA, fats, waxes, pectin	High in BOD, COD, suspended solids (SS), dissolved solids (DS)
Bleaching	Sodium hypochlorite, chlorine, sodium hydroxide, hydrogen peroxide, acids, surfactants, sodium phosphate, short cotton fibre	High alkalinity, high SS
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD, high DS
Dyeing	Dyestuff urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents	Strongly colored, high BOD, DS, DS, low SS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly colored, high COD, oily appearance, SS slightly alkaline, low BOD
Finishing	Inorganic salts, toxic compounds	Slightly alkaline, low BOD

Source: Water Research Commission of South Africa, 2000

1.1.4 Environmental Impacts of Textile Wastewater

Textile mills are major consumers of water and consequently one of the largest groups of industries causing intense water pollution. The extensively use of chemicals and water results in generation of large quantities of highly polluted wastewater. According to the U.S. EPA, about 1 to 2 million gallons of wastewater per day are generated by average dyeing facility in the US, reactive and direct dyeing generating most of the wastewater. Around 10^9 kg and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used extensively in dye and printing industries. Textile processing employs a variety of chemical, depending on the nature of the raw material and products. It is estimate that about 10% are lost in industrial wastewater. The Wastewater generated by the different production steps (i.e. sizing of fibers, scouring, desizing, bleaching, washing, mercerization, dyeing and finishing) has high pH and temperature. It also contains high concentration of organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulfide, sodas, and alkalinity. In addition, the high salt conditions (typically up to 100 g L^{-1}

sodium chloride) of the reactive dye baths result in high-salt wastewater, which further exacerbates both their treatment and disposal.

This wastewater causes serious impacts on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, and oil and grease in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. Effluent from mills also contains chromium, chemicals; effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat. Besides, the improper handling of hazardous chemical content in textile water has some serious impacts on the health and safety of workers. Contact with chemical puts them the high risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and even respiratory problems. Azo type of dyes, because of their toxicity and potentially carcinogenic nature, wastewater originated from dyes production and application industries pose to major threat to the surrounding ecosystems and human health (*Jian-Hui Sun 2006*).

1.1.5 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 1.4.

1.2 Photocatalytic Oxidation of Water Borne Organic Pollutants

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.

Table 1.4: 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

1.2.1 History of Photocatalysis

We are surrounded by photochemistry everyday; we see it in the green color of grass and leave every summer day. However, the first mention of photocatalysis was by Plotnikov in the 1930's in his book entitled Allaemeine photochemie. The next major development followed in the 1950's when Markhani and Laidler performed a kinetic study of photo-oxidation on the surface of zinc oxide in an aqueous suspension. By the 1970's researchers started to perform surface studies on photocatalysts like Zinc Oxide and Titanium dioxide. Titanium Dioxide may come in the anatase or the rutile form. Degussa P25 Titanium Dioxide contains both the anatase and rutile form. Curiously, this mixture long stood as the standard in photocatalysis with high reactivity. In the 1970's solar energy was being studied due to a need for more available renewable resources and environmental concerns; photochemistry was looked upon for the storage and usage of solar energy. In 1972 Fujishima and Honda had a breakthrough for the photolysis of water with a semiconductor electrode, which could also be a solar powered cell. The next big breakthrough in photochemistry occurred in 1976 when Carey and Oliver developed a method for measuring the variation in quantum efficiency with intensity. The interest in using Titania as a photocatalyst has since been revived in the 1990. In the 1980's and 1990's there came an increasing concern for environmental preservation and cleanup. As a result some environmental scientists have looked at photochemistry for air, water, and soil cleanup TiO_2 catalyzed photochemistry can accomplish the mineralization, which is the degradation of organic compounds to H_2O and CO_2 and its inorganic substituents if the organic compound should have any**,** of many different organic compounds.

During the last few years, semiconductor mediated photocatalysis has been reported as a promising route to destroy toxic and hazardous organic substances in industrial wastewater and drinking water. In most cases, a complete oxidative destruction of pollutants has been observed and the end products include CO_2, H_2O and inorganic ions. The harvest of sunlight for photo catalysis has been a tremendous boon to the process, on account of the economic feasibility, ease of large scale operation and process efficiency.

1.2.2 Principle of Photocatalysis

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

$$h^+ + OH^- \longrightarrow OH^\bullet \qquad (2)$$

$$h^+ + H_2O \longrightarrow OH^\bullet + H^+ \qquad (3)$$

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

$$O_2 + e^- \longrightarrow O_2^- \qquad (4)$$

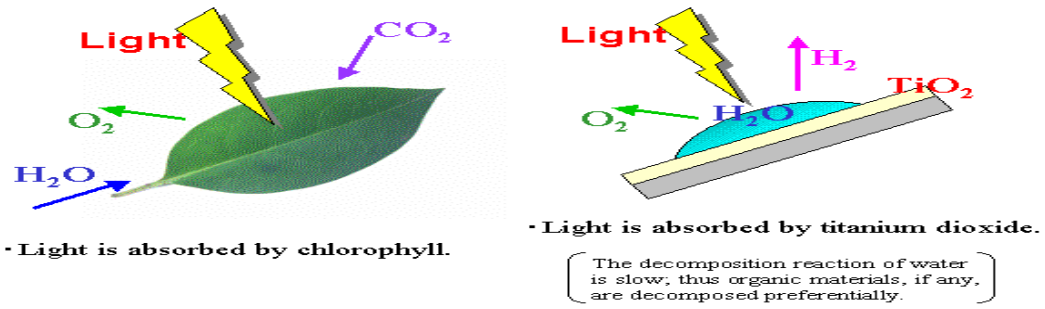

Fig. 1 The photosynthetic reaction in plants is basically similar to the photocatalytic reaction in titanium oxide.

$$O_2^- + H^+ \longrightarrow HO_2^\bullet \quad (5)$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \quad (6)$$

$$^\bullet O_2^- + HO_2^\bullet \longrightarrow HO_2^- + O_2 \quad (7)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad (8)$$

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

$$H_2O_2 + O_2^{\cdot -} \longrightarrow {>}OH^\cdot + OH^{\cdot -} + O_2 \quad (9)$$

$$H_2O_2 + e^- \longrightarrow {>}OH^\cdot + OH^- \quad (10)$$

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

$$H_2O_2 + h\nu \longrightarrow {\cdot}OH + {\cdot}OH \quad (11)$$

$$\cdot OH + \text{dye} \longrightarrow \text{dye intermediate} \quad (12)$$

$$\cdot OH + \text{dye intermediate} \longrightarrow CO_2 + H_2O + \text{end products} \quad (13)$$

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.

1.2.3 Photocatalyst

A variety of photocatalyst (generally semiconductor oxide or sulphides of some metals) which produce excited high energy state of e^+/h^+ pairs have been employed for decomposition of organic pollutants and dyes [*Siva Kumar and Shanthi, 2001; Vinodgopal and Kamat, 1992*]. Table 1.5 shows the band gap of different semiconductors. Among various semiconductor materials tested under similar conditions for the degradation of organic compounds, titanium dioxide (TiO_2) has been demonstrated to be most active photocatalyst. *Daneshvar et. al., 2004* reported that zinc oxide (ZnO) is a suitable alternative to TiO_2 since its photodegradation mechanism has been proven to be similar to that of TiO_2.

Many other semiconductor particles like cadmium sulphide (CdS) or Gap absorb large fraction of the solar spectrum and can form chemically activated surface bond intermediates but unfortunately these photocatalyst are degraded during the repeated catalytic cycles involved in the heterogeneous photocatalysis. Titanium dioxide's strong resistance to chemical and photo corrosion, its safety and low cost and biological harmless limits the choice of convenient alternative [*Pelizzetti, 1995*]. Moreover TiO_2 is more stable than the other photocatalyst in ambient condition and can be recycled [*Kiriakidou et al., 1999; Sun and Smirniotis, 2003*]. Furthermore, TiO_2 has a special feature that it can use natural UV due to appropriate energetic separation between its valence and conduction bands which can be surpassed by the energy content by a solar photon. Therefore, degradation of the organic pollutants present in wastewater using irradiated TiO_2 suspension is the most promising process. Anatase and rutile are two forms of TiO_2 being frequently studied. Rutile form of TiO_2 is claimed as a catalytically inactive or much less active form. However, Degussa P25, which has both anatase and

rutile forms with ratio of anatase to rutile equal to 3-4/1 is one of the best TiO_2 photocatalyst and used frequently as abenchmark in photocatalysis. It has been shown in numerous studies that there is positive interaction of anatase and rutile TiO_2 particles of Degussa P25, which enhances the electron hole separation and increases the total photo efficiency [*Sun and Smirniotis*].

According to various reports, mainly from laboratory scale investigation, slurry type reactors seem to be more efficient than those based on immobilized catalyst *[Bideau et. al., 1995; Murabayashi et. al., 1993; Chester et.al., 1993]*. However for engineering application, there is an intrinsic drawback to the first option: the need of a post radiation treatment of particle fluid separation, for catalyst recycling and for the ultimate goal of obtaining a clean, powder free water. Coupled semiconductor offer another possibility to enhance the photo activity because of increase in the separation between charges and then reduce the energy (increasing wavelength) necessary to excite the system. The photocatalyst such as titanium dioxide and zinc oxide could be easily separated from the treated effluents by Filtration/Centrifugation and could be reused repeatedly without much loss in their photocatalytic activity.

Table 1.5 Band Position of Some Common Semiconductor Photocatalyst in Aqueous solution at pH=1

Semiconductor	**Valence Band (V vs NHE)**	**Conductance Band (V vs NHE)**	**Band gap (eV)**	**Band gap Wavelength (nm)**
TiO_2	+3.1	-0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387
ZnS	+1.4	-2.3	3.7	335
WO_3	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	496
CdSe	+1.6	-0.1	1.7	729
GaAs	+1.0	-0.4	1.4	886
GaP	+1.3	-1.0	2.3	539

1.2.4 Fundamentals of Titanium Dioxide Photocatalysis

It is known that photocatalysts can be either homogeneous or heterogeneous. In a system where a homogeneous photocatalyst is used, the photocatalytic reaction takes place in a homogeneous liquid phase. Examples of such photocatalysts include dye, soluble metal catalysts like copper complexes, tin chloride, palladium chloride, Fenton reagent and hydrogen peroxide. On the other hand, if a heterogeneous photocatalyst is used the photocatalyst and reactant are present in different phases and the photocatalytic reaction occurs at their interface. Examples of heterogeneous photocatalysts include poiyoxometallates such as $Cs_3PW_{12}0_{40}$, TiO_2, in the colloidal and powdered form or dyes supported on glass, sand and other materials. Solid TiO_2 absorbs light in the near UV (-350 nm) causing an electron from the valence band to be excited across the band gap of +3.0 eV up to the conduction band containing free electrons.

Catalyst (TiO_2) has the ability to produce conductivity similar to that of metals. The carriers may be trapped at or near the TiO_2 particle surface; thus, enabling electron transfer reactions across the interface with a large variety of organic molecules absorbed on the TiO_2 surface from the solution. The potential of the trapped hole carrier is +3.2 V and the electron has a potential of on the hydrogen scale. This makes the hole a powerful oxidizing agent and the electron a good reducing agent. The hole can generate a hydroxyl radical at the surface or a one electron oxidation of a wide range of adsorbed organic molecules can be initiated.

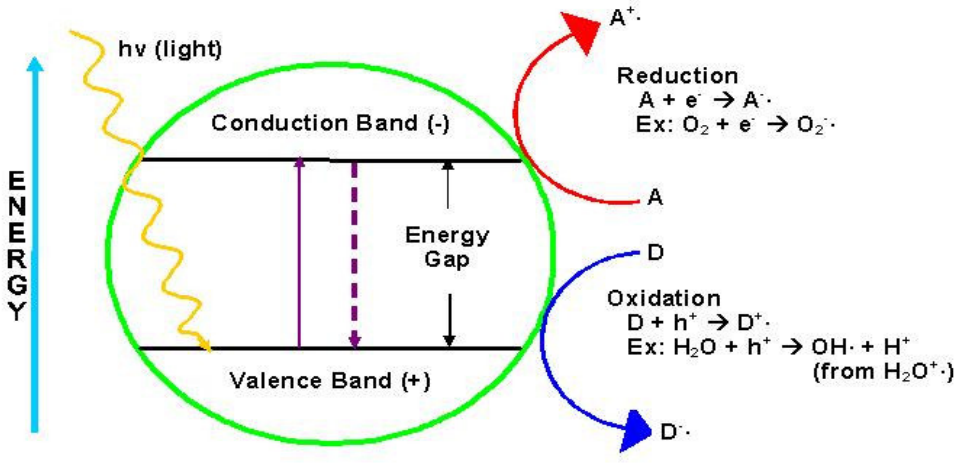

Fig- 1.2.1 Irradiated TiO_2 particle

The electron is captured by O_2 to generate the reactive super oxide ion. For the above reasons the illuminated TiO_2 surface is an extremely attractive catalyst for the initiation of the oxidation of a wide range of organic compounds. In most cases the oxidation can proceed to mineralization where the final products are CO_2, H_2O and inorganic ions of other elements that may be present in the organic molecule. As stated earlier the difficulty of handling the material due to the fine particulate nature of TiO_2 along with a relatively high electrical energy cost because the quantum yield is a bit too low, has limited the commercialization and widespread use of this technology.

1.3 THE POWER OF LIGHT

Light is one of the various electromagnetic waves present in space. The electromagnetic spectrum covers an extremely broad range, from radio wavelength of a meter or more, down to x-rays with wavelengths of less than one billionth of a meter. The UV-visible portion occupies an intermediate position, having both wave and particles in varying degrees (Figure-1.3.1).

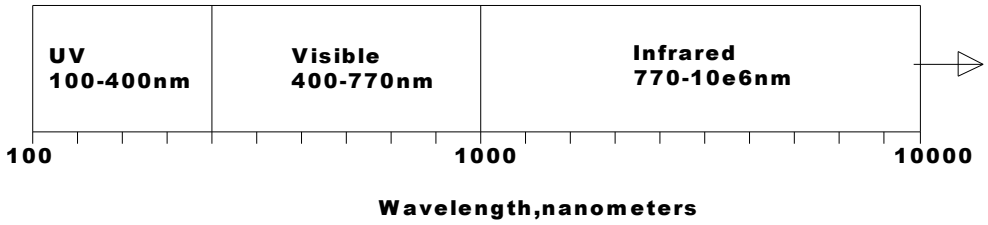

Fig- 1.3.1 The Optical Portion of Electromagnetic Spectrum

1.3.1 Ultraviolet (UV) Light

Ultraviolet radiation (UV) is radiation whose wavelength is shorter than the violet end of the visible spectrum. Being very energetic, UV can break chemical bonds, making molecules unusually reactive or ionizing them, in general changing their mutual behavior. Short wavelength UV light exhibits more quantum properties than its visible or infrared counterparts. UV light is arbitrarily broken down into three bands. UV-A (315-400 nm),which is the least harmful type of UV light, as it has the least energy, is often called black light, and is used for its relative harmlessness and its ability to cause fluorescent

materials to emit visible light-thus appearing to glow in the dark. UB-B (280-315nm) typically the most destructive form of UV light because it has enough energy to damage biological tissues and UV-C (100=280nm) is almost completely absorbed in the air within a few hundred meters. The Sun emits a large amount of UV radiation, which could quickly turn Earth into a barren desert; however, most of it is absorbed by the atmosphere's ozone layer before reaching the surface. The electromagnetic spectrum of ultraviolet light can be subdivided in a number of ways. The draft ISO standard on determining solar irradiances (ISO-DIS-21348) describes the following ranges shows the subtypes of ultraviolet light in Table 1.6.

Table 1.6 Shows the Subtypes of Ultraviolet Light

Name	Abbreviation	Wavelength range in nanometers	Energy per photon
Ultraviolet A, long wave, or black light	UVA	400 nm - 315 nm	3.10 - 3.94 eV
Near	NUV	400 nm - 300 nm	3.10 - 4.13 eV
Ultraviolet B or medium wave	UVB	315 nm - 280 nm	3.94 - 4.43 eV
Middle	MUV	300 nm - 200 nm	4.13 - 6.20 eV
Ultraviolet C, short wave, or germicidal	UVC	280 nm - 100 nm	4.43 - 12.4 eV
Far	FUV	200 nm - 122 nm	6.20 - 10.2 eV
Vacuum	VUV	200 nm - 10 nm	6.20 - 124 eV
Extreme	EUV	121 nm - 10 nm	10.2 - 124 eV

1.3.2 Visible Light

Visible light is concerned with the radiation perceived by the human eye having wavelength (λ) range of 400-770 nm. The lumen (lm) is the photometric equivalent of the watt, weighted to match the eye response of the "standard observer". Yellowish-green light receives the greatest weight because it stimulates the eye more than the blue or red light of equal radiometric power (1W at 555 nm=683.0 lumen).

1.3.3 The Solar Spectrum

Of all the energy coming from that huge reactor, the sun, the earth receives $1.7x10^{14}$ kW, meaning $1.5x10^{18}$ kWh per year. Fig- 3.3 shows the standards solar radiation spectra at ground level on a clear day (*Hulstrom et al., 1985*). The dotted line corresponds to the extraterrestrial radiation in the same wavelength interval.

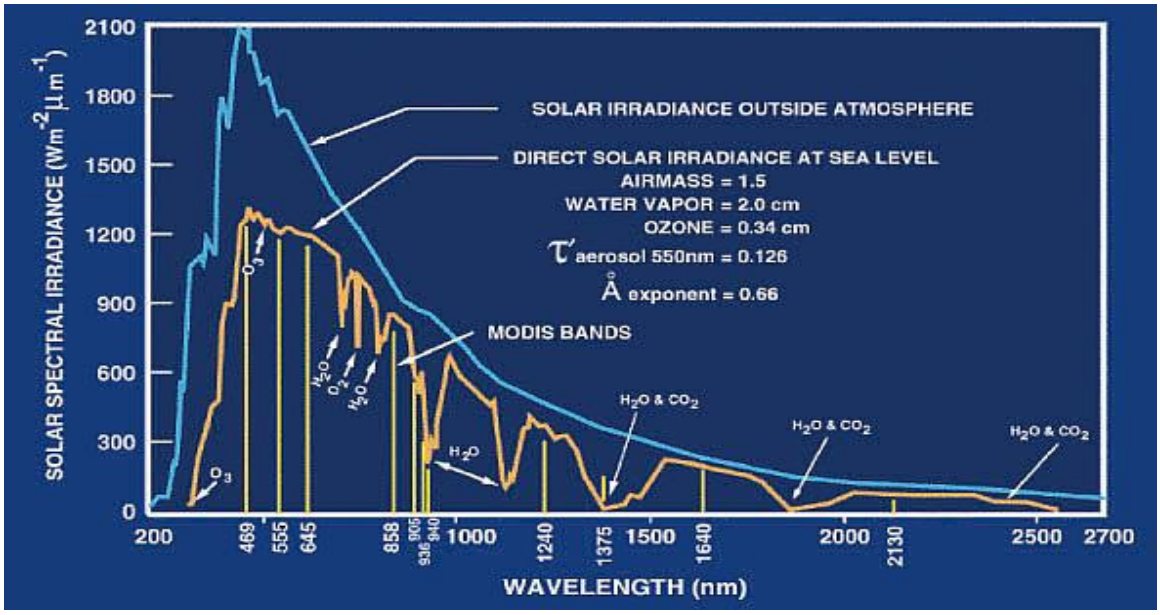

Fig- 1.3.3 - Solar radiation measured above the atmosphere and at the surface.

Solar ultraviolet radiation, as explained above is, only a very small part of the solar spectrum (between 3.5% to 8%).However this ratio may be different for a given location on cloudy and clear days. The percentage of global UV radiation (direct+diffuse)

generally increase with regard to total global when atmospheric transmissivity decrease mainly because of clouds, aerosols and dust etc. in fact, the average percentage ratio between UV and total radiation on cloudy days is up to two percentage points more than values on clear days.

1.4 OBJECTIVES OF PRESENT STUDY

Main objective of my study is to treat those recalcitrant /non-biodegradable compounds present in textile wastewater which are not treated by conventional treatment processes. In an attempt to increase the efficiency of decomposition of the impurities present in the wastewater and to improve the economics of the process, the work was carried out on the degradation of Procion Blue dye and textile effluents containing dyes using photocatalytic treatment. A single dyeing operation can use a number of dyes from different chemical classes resulting in a mixed wastewater of varying characteristics. The description of textile effluent color in terms of absorbance is more useful than dye concentration, as different dyes give rise to different intensities and colors. The wastewater used in this study was treated effluent from the textile dyeing industry near by Ambala. During this project, color levels in samples of the WWTP final clarifier effluent delivered to the environmental laboratories where this study was conducted were consistently greater than the permissible color levels.

Advantages of photocatalytic treatment are that it does not transfer pollutants from one phase to another and it will lead to complete mineralization of organic compounds. The study was undertaken with the following objectives:

- Characterization of effluent
- Photocatalytic treatment for model dye compound and real effluent
- Study of effect of variables on photocatalytic efficiency and its optimization

CHAPTER-2

Literature Review

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. In order to meet the stringent international standards, treatment of industrial wastewater is mandatory. Heterogeneous photocatalysis is a process of great potential for pollutant abatement and waste treatment. In order to improve the overall performance of the photo process, heterogeneous photocatalysis is being combined with physical or chemical operations, which affect the chemical kinetics and/or the overall efficiency. This review addresses the various possibilities to couple heterogeneous photocatalysis with other technologies to photo degrade organic and inorganic pollutants dissolved in actual or synthetic aqueous effluents (*Vincenzo Augugliaro et al., 2006*). A survey of literature was carried out to know the latest advancements in the field of heterogeneous photocatalysis for the treatment of dyes and textile wastewater.

2.1 PHOTOCATALYTIC TREATMENT

The UV-induced photocatalytic degradation of two azo dyes, Methyl Red and Methyl Orange, has been carried out in aqueous media in the presence of oleic acid (OLEA)- and tri-n-octylphosphine oxide (TOPO)-capped anatase TiO_2 nanocrystal powders (mean particle size: 6 nm). Significantly, although all titania catalysts were effective in removing both parent dyes and their related derivatives, the degradation rate by the OLEA-capped TiO_2 nanocrystals was double as that obtained with both its TOPO-capped analogous and TiO_2 P25 Degussa (*R. Comparelli et al. 2005*). Electrochemical-assisted photo degradation of methyl orange has been investigated using TiO_2 thin films. The light sources chosen ranged from ultraviolet to visible light. The effect of agitation of the solution at different speeds has also been studied (*Zulkarnain Zainal et al. 2005*). The photo catalytic activities of the coupled ZnO/SnO_2 photo catalysts, evaluated using the photo degradation of methyl orange as a probe reaction, were also found to be related to the calcinations temperatures and the Sn contents. The photo-stability of the ZnO/SnO_2 photo catalyst was also studied (*Cun Wang et al., 2004*).

Yingxu Chen et al. (2005) investigated the role of these primary oxidants in the photo degradation of an azo dye, Acid Orange 7 (AO7) in UV-illuminated TiO_2

suspension. Little influence of methanol or isopropanol on the degradation was found. Due to the reciprocity of loading TiO_2 and activated carbon, the TiO_2/AC prepared showed high photo activity for the photo oxidation of methyl orange. it was observed that TiO_2/AC has higher decomposition efficiency than pure TiO_2 particles, as well as a mixture of TiO_2 powder with activated carbon (*Youji Li et al., 2005*). The Ethyl Violet (EV) can be degraded efficiently in aqueous TiO_2 dispersions by visible light irradiation. The UV–vis spectra changes during the photodegradation of EV in the aqueous TiO_2 dispersions under visible light irradiation. After irradiation for 68 h, ca. 99% of EV was degraded. During visible irradiation, the characteristic absorption band of the dye decreased rapidly and shifted to lower wavelength but no new absorption bands appeared even in the ultraviolet range ($\lambda > 200$ nm),(*C.C. Chena et.al., 2005*).

The photocatalytic organic content reduction of synthetic municipal wastewater has been studied at pilot plant scale. The solar photocatalytic has been implemented in paper and pulp mill for water detoxification, as pulp effluent contains polyphenolic polymer lignin-non-biodegradable substances. The photocatalytic degradation of dimethoate, an organophosporous pesticide has been investigated (*S.K.Dubey et. al., 2006*).

Bekkouche et al. (2004) studied the adsorption of the micro pollutant on the photocatalyst, mainly the titanium oxide anatase form, is a determining stage in the process of photo degradation. An experimental study carries out the adsorption of phenol, chosen as the model pollutant, on a photocatalyst, titanium oxide anatase (Degussa P25). The aggregation effect of TiO_2 in aqueous solution had an optimal concentration of the catalyst for a concentration of phenol. The adsorption was optimal for a pH between 5 and 6 in the neighborhood of the isoelectric point of TiO_2.*Damien Gumy, 2006* has been investigated the factors influencing photocatalytic drinking water detoxification and disinfection by suspended and fixed TiO_2.

2.2 DEGRADATION OF DYES

The photocatalytic degradation has been emerging as a potentially powerful and versatile method for dealing with the problem of wastewater containing different dyes. A number of research groups have dealt with photocatalytic decomposition of this class of materials in the presence of UV-A or visible light with very encouraging results [*Zhang et al., 1998; Vinodgopal and Wynkoop, 1996; Davis et al., 1994*]. With the aim of elucidating the potential applications of advantageous photocatalytic processes, the kinetic and mechanistic aspects of dye design have been investigated and reported in literature [*Galindo et al., 2002; Bauer et al., 2001; Houas et al., 2001*].

Wastewater containing dyes can be treated biochemically in combination with photocatalytic, chemical, thermo chemical and physico chemical treatment methods [*Zhang et al., 1997; Gopalakrishan and Mohan, 1997; Subrahmanyam, 1996; Nasr et al., 1996; Lakshmi et al., 1995; Zang et al., 1995; Vinodgopal and Kamat, 1995; Vinodgopal et al., 1994; Subrahmanyam, 1987*]. The photocatalytic decolorization of reactive orange 16, a textile azo dye, in aqueous heterogeneous solutions containing TiO_2 as a photo catalyst was explored by *Poulious and Aetopoulou, 1999*. Various commercial photo catalysts were compared with respect to their decolorization efficiency and production of co_2. The effect of pH and H_2O_2 on the reaction was ascertained. *Gomathi Devi and Krishnaiah, 1999* investigated the photocatalytic degradation of two azo dyes (p-amino-azo-benzene and p-hydroxy-zo-benzene) using heat treated TiO_2 as the photocatalyst. Anatase form (TiO_2 annealed at 600˚c-650˚c) has proved to be efficient catalyst as compared the ruitle form (annealed at above 700˚c) and also to Degussa P-25 sample for the degradation of these dyes.

Zhao, 2000 examined the direct photocatalytic degradation of dye pollutant sulfordamine B(SRB) in aqueous TiO_2 dispersions and compared to the photosensitization process. The mineralization extent of SRB degradation, the formation of intermediates and final products were monitored to assess the degradation pathways caused by direct photocatalysis. *Sivakumar and Shanthi, 2001* reported the decolorization of reactive textile dyes namely procion brilliant orange M-2R (PBO), procion brilliant magenta M – B(PBM), and procion brilliant yellow M-4G (PBY) using TiO_2 semiconductor as catalyst under sunlight illumination.

Chakrabharti and Dutta, 2004 explored the potential of a common semiconductor, no as an effective catalyst for the photodegradation of two model dyes: Methylene Blue and Eosin Y. The effect of parameter like catalyst loading, initial dye concentration, air flow rate, UV irradiation intensity and pH on the extent of photodegradation have been investigated. *Bouras et al., 2004* demonstrated the photodegradation of basic blue by highly efficient nanocrystlline titania films. Transparent nanocrystallin titania films were deposited on glass slides by using sol-gel procedure carried out in the presence of surfactants, triton X-100. Films were calcined at 550°c to ensure destruction of all organic residues. These films were found to be very efficient for photodegradation of basic blue dye, in aqueous solutions.

Konstantinou and Albanis, 2004 reviewed the photocatalytic degradation of azo dyes containing dtionalities using TiO_2 as photo catalyst in different functionalities using TiO_2 as photocatalyst in aqueous solution under solar and UV irradiation and stated that the mechanism of the photodegradation depends on the irradiation used. Charge injection mechanism takes place under visible irradiation whereas charge separation occurred under UV light irradiation. *Daneshvar et al., 2004* reported that ZnO appears to be a suitable alternative to TiO_2 since its photodegradation mechanism has been proved to be similar to that of TiO_2 for acid Red 27.

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.

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*).

Sumandeep Kaur et.al., 2007 reported the accelerated sonophotocatalytic degradation of Reactive Red (RR) 198 dye under visible light using dye sensitized TiO_2 activated by ultrasound. The effect of sonolysis, photocatalysis and sonophotocatalysis under visible light has been examined to study the influence on the degradation rates by varying the initial substrate concentration, pH and catalyst loading to ascertain the synergistic effect on the degradation techniques. A comparative study using TiO_2, Hombikat UV 100 and ZnO was also carried out. This methodology has additional advantage for harnessing the visible component of the solar energy for the degradation of organic pollutants in water.

A comparative study between the photocatalytic and sonophotocatalytic oxidation process of congo red was carried out using titanium dioxide as a catalyst. The effect of a number of parameters, such as the initial concentration of dye, the presence of oxygen and ultrasound, the TiO_2 crystalline structure and the amount of TiO_2, was studied using an inexpensive reactor. In the second part of this document, the oxidation and reduction processes of methyl orange was studied using the same reactor, but by changing the chemical environment in order to drive either the oxidation or the reduction reaction. On the other hand, the electrochemical experiments showed that the current densities for the oxidation process of the azo dyes were higher when a conducting glass electrode covered with a thin film of TiO_2 was used as a working electrode instead of a platinum electrode, showing that the TiO_2 electrode is not passivated by the oxidation reaction. The photo catalytic oxidation rate of aqueous solutions of congo red and methyl orange shows a remarkable increase when it is carried out in the presence of ultrasound.

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*).

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).

2.3 TREATMENT OF TEXTILE WASTEWATER

A. Alinsafi et. al.,2007 have applied photo catalysis with TiO_2 particles immobilised either on a glass slide or on a non-woven glass fiber fabric has been applied to pure reactive dyes' (azoïc and metal phthalocyanines) solutions as well as textile wastewater containing the same dyes under UV and solar irradiation. Decolourization of textile wastewater was in the range 21–74% under solar irradiation, with COD removal rate between 0.2 and 0.9 g COD/h/m^2.. Performance prediction is therefore difficult but the results are encouraging for textile wastewater remediation. No pH adjustment is

necessary and wastewater at high pH can be treated directly after suspended solids removal.

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

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

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

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

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

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

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

Photo degradation of a real textile dyeing wastewater taken from Hilla textile factory in Babylon Governorate, Iraq have been investigated. Photocatalytic degradation was carried out over suspensions of titanium dioxide or zinc oxide under ultraviolet irradiation. Photodegradation percentage was followed spectrophometrically by the measurements of absorbance at max equal to 380 nm. The rate of photo degradation

increased linearly with time of irradiation when titanium dioxide or zinc oxide was used. A maximum color removal of 96% was achieved after irradiation time of 2.5 hours when titanium dioxide used at 303K and 82% color reduction was observed when zinc oxide used for the same period and at the same temperature. The effect of temperature on the efficiency of photodegradation of dyestuff was also studied. The activation energy of photodegradation was calculated and found to be equal to 21 ± 1 kJ mol-1 on titanium dioxide and 24 ± 1 kJ mol-1 on zinc oxide (*Abbas J. A. et. al., 2008*).

The oxidative degradation of an actual textile dye house wastewater was investigated by means of photocatalysis in the presence of TiO_2. The UV-A-induced photocatalytic oxidation over TiO_2 suspensions was capable of decolorizing the effluent completely, as well as reducing chemical oxygen demand (COD) sufficiently (COD reduction generally varied between about 40% and 90% depending on the operating conditions) after 4 h of treatment. Two crystalline forms of TiO_2, viz. anatase and rutile, were tested for their photocatalytic activity and anatase was found to be more active than rutile. The extent of photocatalytic degradation was found to increase with increasing TiO_2 concentration up to 0.5 g/L TiO_2, above which degradation remained practically constant, reaching a plateau. Furthermore, textile effluent degradation was enhanced at acidic conditions (i.e. pH ¼ 3) and in the presence of hydrogen peroxide. To assess catalyst activity on repeated use, experiments were performed where the catalyst was recovered and reused; after three successive uses, TiO_2 had sufficiently retained its photo catalytic activity. Finally, the luminescent marine bacteria Vibrio fischeri was used to assess the acute ecotoxicity of samples prior to and after the photocatalytic treatment and it was found that ecotoxicity was fully eliminated following photocatalytic oxidation (*Pantelis A. Pekakis et.al., 2006*).

Several systems are used in photocatalytic degradation; two of them are experimented in the treatment of textile dyes and washing out reagents. The Thin Fixed Film Bed Reactor (TFFBR) and Aerated Cascade photocatalytic reactor ACP models developed to investigate photocatalytic degradation of organic compounds. For the first one the catalyst is fixed while, for the second one the catalyst is hanging in the solutions. The efficiency of the two systems are tested for the solar catalytic treatment of commercial dyes and washing out reagents. The degradation of the black, red, blue and

golden dyes shows that the black had the highest TOC degradation than others. Moreover the ACP system was more efficient than TFFBR. The treatment of the washing out reagents in suspended solutions and TFFBR reactor gives a high TOC degradation with the last system comparing to the first one (*Ghozzi K. et.al.,2002*).

CHAPTER-3

Material and Methods

As described in this chapter are the materials and methods used during this research, including the chemicals, glassware instrument like the UV photo reactor, pH adjustment and analysis by UV-Vis Spectrophotometer, COD digester, Electrical conductivity (EC) measurement, and procedures used to treat the dye and effluent solutions with the UV/TiO_2 catalysis and UV/TiO_2/H_2O_2. The compilation of the varying pH of solution, TiO_2 dosages and the varying UV contact times for the Procion Blue dyes with varying concentrations and textile effluents make up the experimental matrix.

3.1 MATERIALS

3.1.1 Dye

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 208nm, 280nm and 616nm. Molecular structure of Procion blue dye is illustrated in Fig-3.1.1. 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:

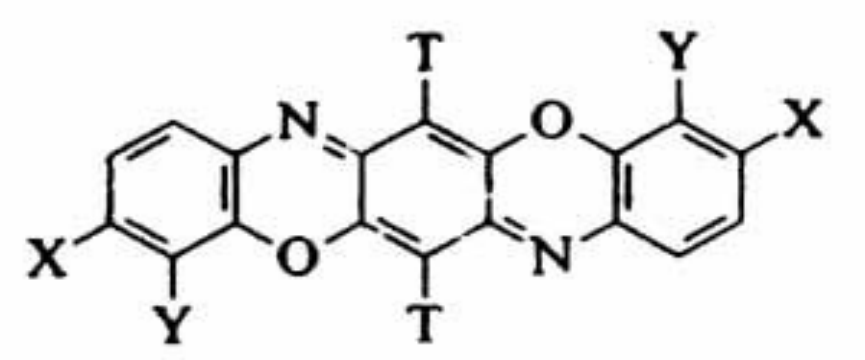

Fig- 3.1.1 Structure of Procion blue dye

3.1.2 Textile Wastewater

Textile wastewater was collected from the industry situated nearby Ambala region. Textile wastewater is analyzed for some initial parameter and treatment was done by photo catalytic treatment.

3.1.3 Reagents and Chemicals Used

The photocatalyst TiO_2 (P25) was procured from Degussa Company. Hydrogen peroxide was used as an oxidant. Textile effluent is characterized for pH, EC, Turbidity, BOD, COD, TDS, TSS, Color etc. For the determination of BOD, phosphate buffer, Calcium chloride, Magnesium sulphate, Ferric chloride, Magneous sulphate, Potassium iodide, Sulphuric acid, Sodium thiosulphate and Strach as an indicator were used. COD of industrial effluent and treated sample was determined by using potassium dichromate solution (Containing Mercuric sulphate and Concentration Sulphuric acid), COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and Ferroin indicator. 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 and textile wastewater.

3.2 INSTRUMENT USED

3.2.1 pH meter

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

3.2.2 Electrical conductivity meter

EC of the samples was determined by using a deluxe conductivity meter model 601 E (Microsil, India). The EC in (mS/cm) of wastewater sample was estimated and before estimation EC meter was calibrated.

3.2.3 Turbidity meter

Turbidity of the samples was measured by Radio Turbidometer, Hatch turbidity was measured as per standards method No. B 2130, page No 2-13, from STANDARD METHODS for the examination of water and wastewater 1989 (17^{th} edition).

3.2.4 Magnetic Stirrer

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

3.2.5 Air sparger

Air is continuously supplied during experiments in UV reactor as well as solar experiments in order to oxidize the organic matter.

3.2.6 Photoreactor

Photo catalytic treatment of dye and effluent were performed in batch experiments. For photocatalytic UV reactor was used which was rectangular having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of iron. Roof of the reactor was made up of wooden; seven UV tubes (36 Watt each) were attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Four magnetic stirrers were fitted in the reactor to carry out the photo catalytic reaction in slurry mode. Two different view of photoreactor are shown in Fig. - 3.2.1 a and 3.2.1 b.

3.2.7 Filtration

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

3.2.8 COD Digester

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

Fig- 3.2.1 a Outer view of photoreactor

Fig-3.2.1 b Photoreactor at lab level during photocatalytic treatment

3.2.9 Radiometer

Intensity of UV and solar light was measured with Eppley radiometer.

3.2.10 Reaction vessel

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

3.2.11 Spectrophotometer

The spectrum was taken with UV-vis. Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer).

Fig-3.2.3 Glass bowl reactor with magnetic stirrer at lab scale

3.3 METHODS

3.3.1 Collection and storage of wastewater and dye sample

Sample was collected from homogenous tank of effluent treatment plant of textile industry. Sampling vessel was cleaned and rinsed carefully with distilled water and then washed with sample during sample collection. Then effluent was stored in cold store at 4°C within 3 to 4 hrs of collection. Dye sample was also collected from same industry which is basically used in the dyeing processes and stored in dry place protected from moisture.

Wastewater sample was analyzed for the COD, BOD, TDS, TSS, Color, Turbidity, pH, EC, Turbidity etc. The entire experimental test was repeated to get reproducibility of results. Parameters were analyzed by methods given in standard methods for the examination of water and wastewater 1989 (17^{th} edition). Reagents used for the present investigation were of AR Grade and single distilled water was used throughout the study.

3.3.2 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 25 ppm 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. If this solution is diluted ten times then 1 ml contains 30

mg of H_2O_2. Hence for adding 300 mg/l of H_2O_2 in dye or effluent, add 10 ml in 1 L of dye or 1 ml of diluted peroxide solution in 100 ml of dye solution.

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).

3.3.3 Color measurement by Pt-Co method

. The value of color is pH dependent so color in this test is reported at 7.0 pH. The maximum absorbance of textile wastewater was found at 530 nm wavelength during full scan. So the initial and final absorbance was measured at this wavelength using spectrophotometer (*M.Tech Thesis*). The optical density (OD) of the reference solution and sample was measured at corresponding wavelength and the values were reported in PCU i.e. platinum cobalt unit using following formula:

Color units = OD*500/0.132

3.3.4 Estimation of COD

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

3.3.5 Estimation of BOD

BOD was estimated as per standards method No. 5210 B, page No.5-4 from STANDARD METHODS for the examination water and wastewater, 1989(17^{th} edition).BOD was estimated by BOD bottle method.

3.3.6 Total dissolved solids (TDS)

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

3.3.7 Total suspended solids (TSS)

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

3.3.8 UV intensity measurement

UV intensity was measured in the UV reactor with the help of radiometer. Radiometer was placed at different places from top with variation in distance from UV tubes such as top of the reactor, bottom of the reactor and middle of the reactor. It has been observed that the maximum UV intensity was at the middle of the UV reactor which was measured to be 25 W/m^2.

3.3.9 Analysis for decoloration/degradation

The decolorisation/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^oC.Full scan was taken after treatment for the PB dye as well as effluent.

3.4 PHOTOCATALYTIC TREATMENT

Photocatalytic treatment was done for Procion blue dye as well as textile effluent sample. The dyes as well as effluent of textile industry were treated and the various

parameters like pH, catalyst dose, concentration of oxidant, initial concentration of dye were varied and optimized.

3.4.1 Degradation of dye

Procion blue dye solution 25 ppm 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.

3.4.2 Degradation of textile effluent

Wastewater collected from the homogenous tank of effluent treatment plant (ETP) of textile industry was highly polluted and its characteristics are shown in Table 4.1. So to get the value within measurable range, sample was diluted twice. Single distilled water was used for the all dilutions. Initial pH of sample was checked and varied all the parameter to optimize the value of pH, catalyst dose, oxidant concentration and comparison of photocatalytic activity with solar light. 200 ml of sample taken in glass bowl (1000ml quantity) and bowl was covered with transparent thin foil; air is also supplied by the aerator during experiments. Wastewater sample was treated in the presence of UV light in photo reactor for four hours. Sample was withdrawn in every 20 min., filtered through the syringe filter and absorbance was taken in spectrophotometer. COD of samples was measured as per the standard methods. All tests were repeated for getting the reproducibility of results.

After the photocatalytic and solar photocatalytic treatment of wastewater (with optimized conditions), sample was filtered and it has been analyzed for COD, TSS, TDS, Color pH, EC, Turbidity etc.

CHAPTER-4

Results and Discussions

The photocatalytic treatment using TiO_2 catalyst was employed for the effective degradation of dye solution and textile mill wastewater in batch photo reactor at 298 K. A matrix of experimental variables was developed in which the TiO_2 dose, pH, UV exposure time, dye concentration and use of oxidant were varied and applied to dye solution and textile effluent.

4.1 DEGRADATION OF PROCION BLUE (PB) DYE

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.

The objective was not only complete decolorization but; rather to determine efficient means to degrade the organic constituents and comply with the pollutants discharge norms for textile effluent in term of color and COD. The efficacy of photo catalytic treatment was dependent on the initial color intensity of the test solution, UV exposure time and catalyst as well as oxidant dose.

4.1.1 UV –Vis Spectra of PB Dye

The photocatalytic experiments were conducted under both UV as well as solar light. The decolorization and degradation was recorded in term of change in intensity of characteristics peaks. Procion Blue dye (25ppm) shows the absorption peaks at 280 and 616 nm. Fig. 4.1.1 shows the UV-Vis. Spectra of 25 ppm of PB dye solution. The rate of degradation was recorded with respect to change in intensity of absorption of peaks at 280 nm.

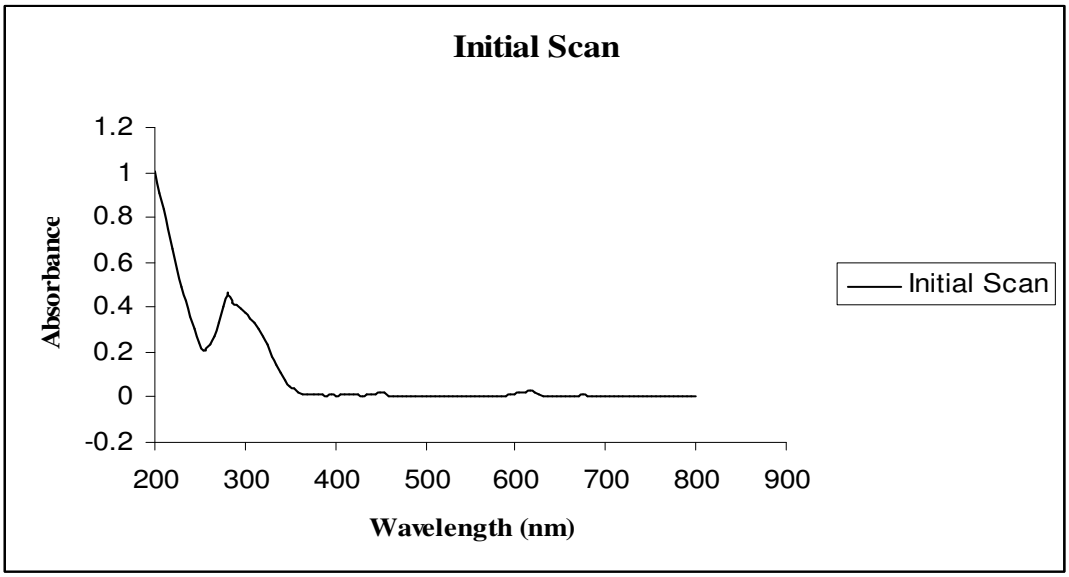

Fig-4.1.1 The full scanning spectrum of Procion Blue (25 ppm) dye solution

4.1.2 Photolysis of Procion Blue Dye

Procion blue dye solution was irradiated under ultraviolet (UV) light alone in the absence of catalyst. Fig- 4.1.2 shows the dye removal efficiency as a function of irradiation time. It was observed that after 200 minute of UV treatment the degradation of dye is not significant as compared to Solar/TiO_2 and UV/TiO_2.*M. Faisal et. al., 2005; W.S.Kuo and P.H.Ho, 2006* have reported the similar behaviour during the photolysis of dye under ultraviolet irradiation.

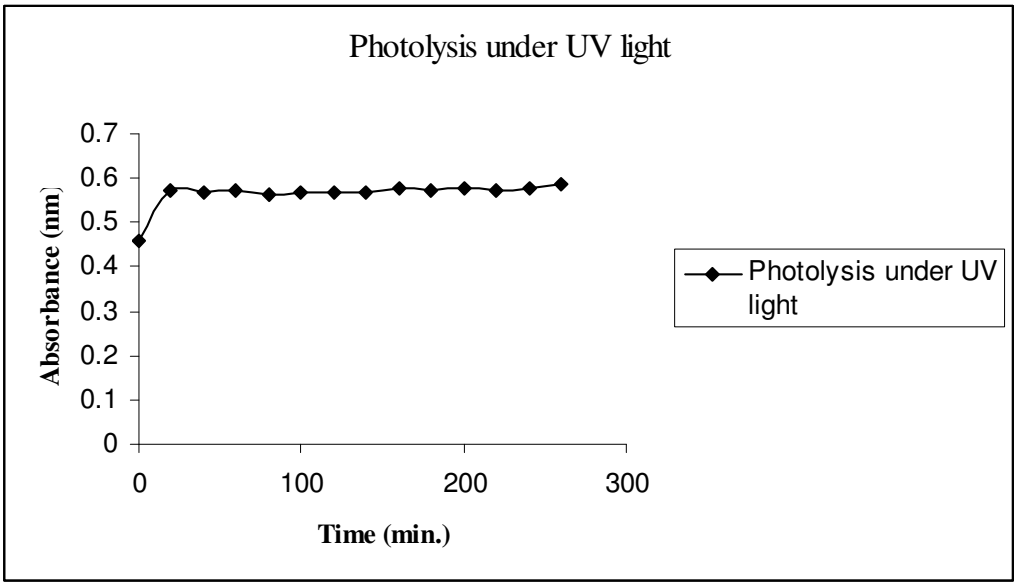

Fig - 4.1.2 Effect of UV light Procion Blue dye (25 ppm), Time = 260 min.

4.1.3 Influence of Initial pH

The influence of the initial pH of the dye solution was studied as pH is considered to be one of the most important parameters that can affect the photo catalytic oxidation process. The initial pH of dye solution was varied from pH 2-12. The studies were carried out with 25 ppm Procion blue dye solution and 500 mg/L of catalyst dose. It is quite evident from the graph (Fig-4.1.3) that as the pH of dye solution changes from alkaline to acidic; the percentage degradation is increasing. In the alkaline pH range the degradation was 45% after 3 hrs of photo catalytic treatment at pH 8.0 while there was no significant degradation at pH 10 and 12. In the acidic condition, when pH is decreased from 6.0 to 4.0, the degradation increased upto 97.17% and then decreased to 54 % as pH is further reduced to 2.0. So the maximum degradation has been found at pH 4.0 after 3 hrs of exposure.

The effect of the solution pH on the degradation rate can be explained mainly by adsorption of dye on TiO_2 surface. In acidic suspensions, the adsorption of dyes on the TiO_2 particles was significantly increased comparing to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge (pzc) of the used TiO_2 (Degussa P-25) is widely reported at pH≈6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution. Because the dye is negatively charged, the acidic solution favors adsorption of dye onto photo catalyst surface.

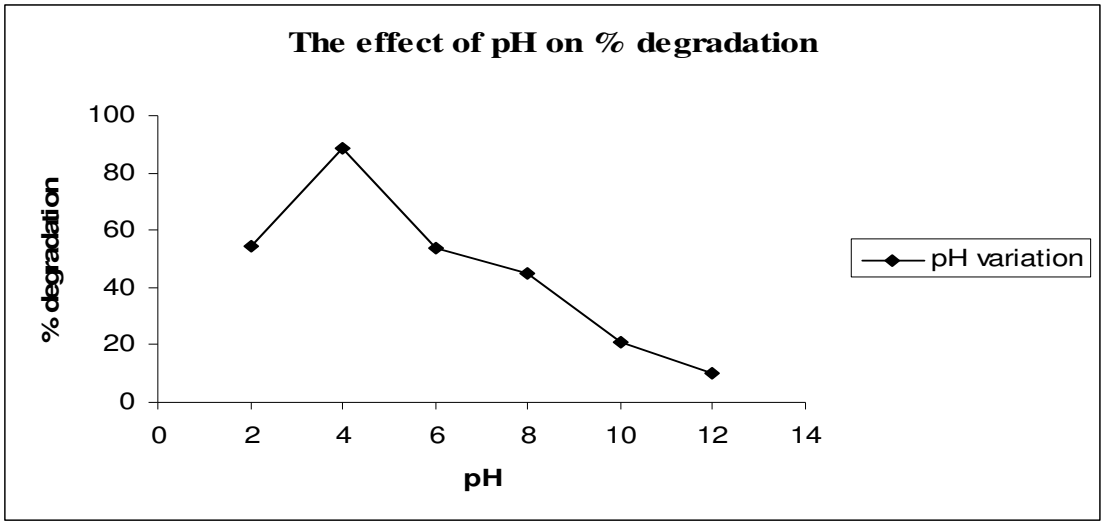

Fig - 4.1.3 Effect of initial pH on photocatalytic degradation of Procion Blue (25 ppm) [TiO_2] = 500 mg/l, Irradiation time=180 min.

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.

4.1.4 Effect of Catalyst Dose

After optimizing pH, the catalyst dose is another important parameter which has strong influence on the degradation kinetics of dye solution. Degussa P-25 TiO_2 catalyst was used in slurry mode. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of TiO_2 catalyst varying from 125 to 750 mg/L, at optimized pH of 4.0 with 25 ppm dye solution and results are presented in Fig-4.1.4. The graph depicts that as the concentration of catalyst increases from 125 to 500 mg/L, the percentage degradation increases from 39% to 88% but increasing the catalyst concentration from 500 to 750 mg/L, the percentage degradation decreases from 88% to 78% respectively. So maximum degradation rate has been observed with catalyst dose of 500 mg/L and it was considered

as the optimum dose for the degradation of procion blue dye solution (25 ppm) for subsequent analysis.

The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. When all the dye molecules are adsorbed on TiO_2 no improvement is achieved by adding more catalyst. The decrease in efficiency, which is observed in the figure, may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of TiO_2 particles. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of TiO_2 which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction.

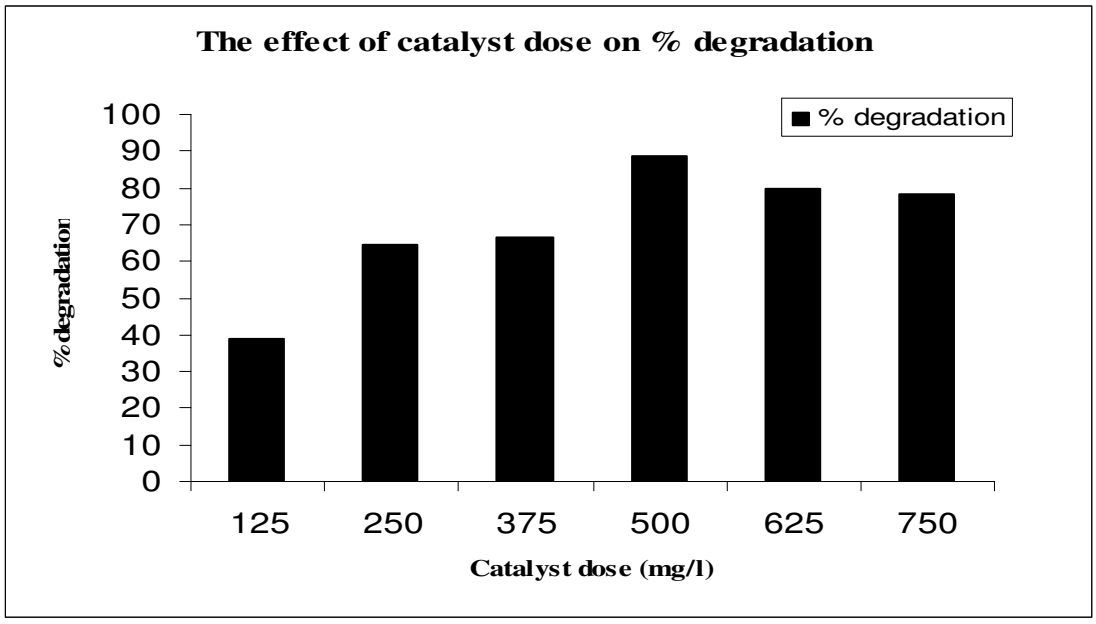

Fig- 4.1.4 Effect of catalyst dose on photocatalytic degradation of Procion Blue [pH] = 4.0, [Procion Blue]$_0$ =25 ppm, Irradiation time=260 min.

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.

4.1.5 Effect of the Initial Dye Concentration

The pollutant concentration is very important parameter in wastewater treatment. The influence of initial concentration of the dye solution has been investigated on the photocatalytic degradation of dye after the optimization of pH and catalyst dose. In order to optimize the catalyst dose the initial dye concentrations was varied during the photo catalytic treatment from 10 to 100 ppm, at constant pH of 4.0 and catalyst dose of 500 mg/L. It has been observed from the graph (Fig- 4.1.5) that increasing concentration of dye solution from 10 to 100 ppm decreases the percentage degradation rate and it was found that at 10 ppm dye concentration, degradation was 90% and at 100 ppm dye concentration, percentage degradation was reduced to 26%. The reason behind this behavior may be due to the increase in the extent of adsorption on the catalytic surface at necessary dye concentration which reduces the catalytic activity of TiO_2. 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 UV-light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency.

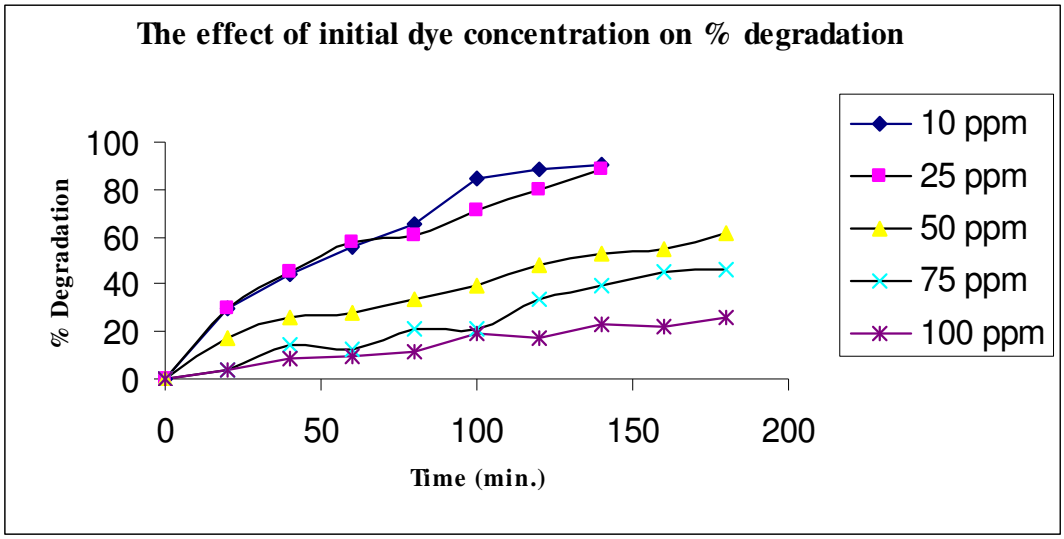

Fig- 4.1.5 Effect of the initial dye concentration on photocatalytic degradation at pH 4.0 & [TiO_2] = 500 mg/l.

Similar results have been reported for the photocatalytic oxidation of different dye by different authors (*M. Muruganandham et. al., 2005; Chin-Chaun Liu et. al., 2006; M. A. Tariq et.al., 2005*.)

4.1.6 Effect of UV Intensity

The influence of light intensity on the degradation efficiency has been examined at constant dye concentration (25 ppm), at pH (4.0) and catalyst loading (500 mg/L). It is evident that the percentage degradation increases with increase in the light intensity as shown in Fig- 4.1.6. The UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photo catalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced.

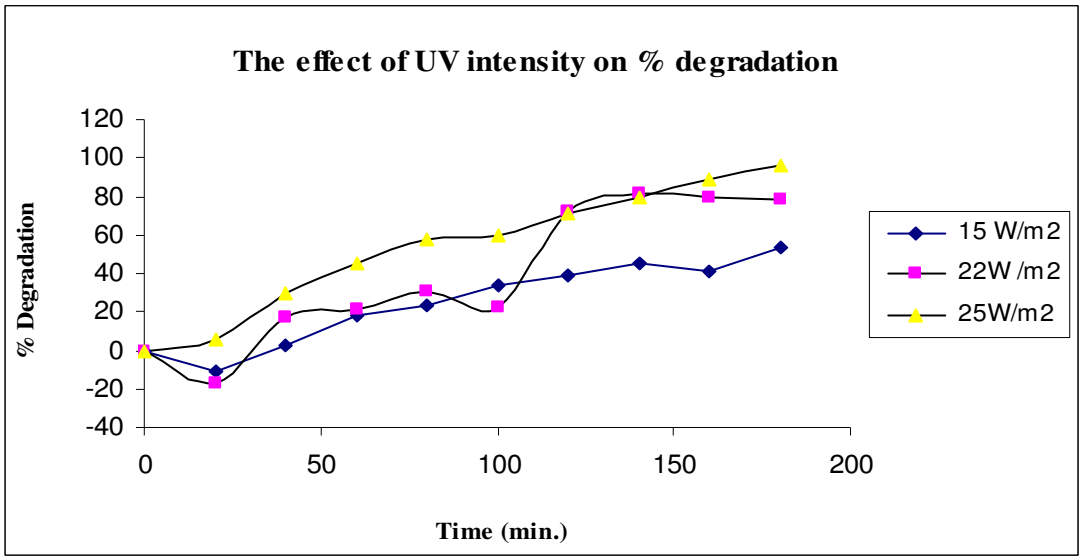

Fig- 4.1.6 Effect of the light intensity on photo catalytic degradation of Procion Blue (25 ppm) at 4 pH & [TiO_2] = 500 mg/l

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.

4.1.7 Comparison of Solar/UV Light

The effect of UV light on the degradation of PB dye by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of dye solution in Solar/UV as well as normal room light. The aqueous suspensions of TiO_2 (500 mg/L)containing Procion blue dyes (25 ppm dye) was exposed to Solar, UV and normal room conditions at pH 4.0. Fig- 4.1.7 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of dye under sunlight, visible and UV light source, respectively. The rate of degradation was found to be slightly more in the UV light in comparison to solar light. After 180 minutes of reaction time the percentage degradation was 82% in solar light and 88% in UV light. It is evident from the graph that percentage degradation of solar light is very close to UV light degradation so solar light can be efficiently used for the photocatalytic degradation of wastewater.

This is due to their ability to absorb part of the visible light, another mechanism of degradation connected with visible light could occur as well. According to this mechanistic approach, the adsorbed dye molecule onto the TiO_2 surface form appropriate excited states due to visible illumination and then these excited states mainly transfer electrons to the conduction band of TiO_2 particles.

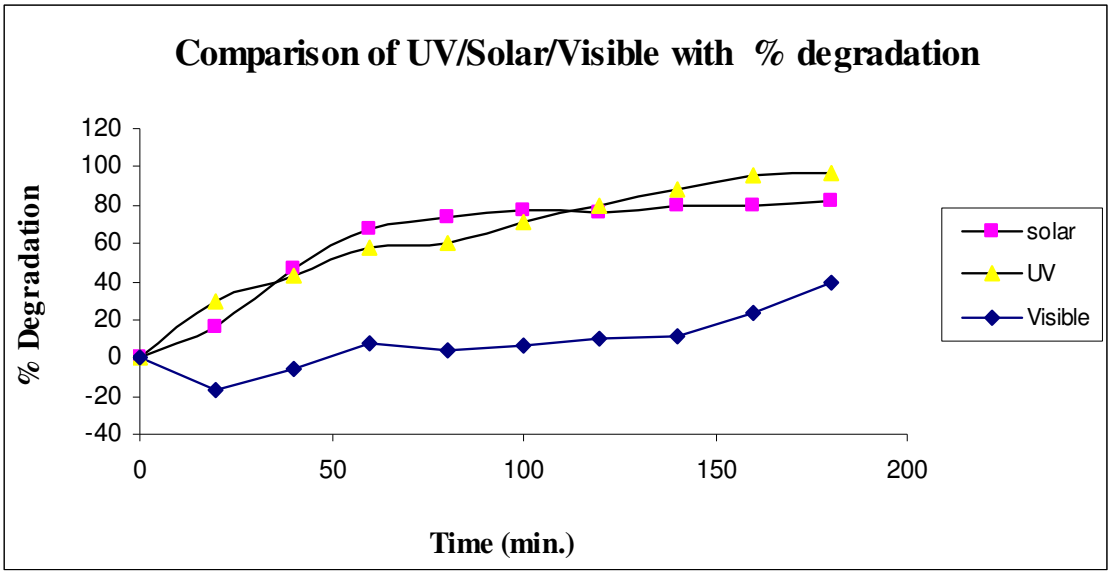

Fig- 4.1.7 Effect of UV/Solar light on photo catalytic degradation of Procion Blue (25 ppm)at 4 pH & [TiO_2] = 500 mg/l.

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.

4.1.8 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 150 to 600 mg/l. Fig- 4.1.8 shows that the rate of photocatalytic degradation of PB dye first increases when hydrogen peroxide concentration was increased upto 300 mg/L, reaching degradation a maximum of 87% but increasing the concentration beyond 300 mg/l, degradation of dye was reduced to 36% after 260 minute of exposure. This dual effect of H_2O_2 can be explained by radical reaction mechanisms. The added H_2O_2 could accelerate the reaction by producing hydroxyl radicals from scavenging the electrons and absorption of UV-light. By addition of excess H_2O_2, it acts as hydroxyl radical or hole scavenger to form the per hydroxyl radicals (HO_2•) which is a much weaker oxidant than hydroxyl radicals.

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.

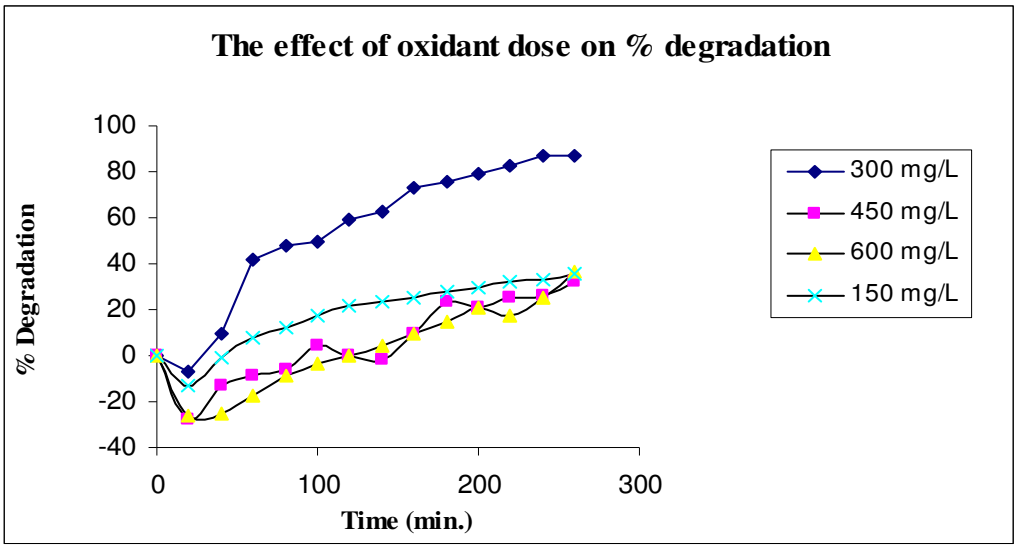

Fig- 4.1.8 Effect of hydrogen peroxide concentration on photocatalytic degradation. Procion Blue (25 ppm) at 4 pH & [TiO_2] = 500 mg/l.

4.1.9 Degradation of Dye During Course of Reaction

Fig- 4.1.9 shows the degradation of Procion Blue dye during the reaction time. The primary absorption peaks of the original dye solution were at 280 nm and 616 nm. As the reaction proceeds, the two peaks disappear gradually and the full scanning spectrum pattern changes obviously after 240 min. This may be the evidence of the intermediate byproduct. At the end of the 240 min of reaction time, there is no evident absorption peak observed. It indicates that the main chromophores in the original dye solution are destroyed with the photo catalytic reaction and proves that Procion Blue is fully decomposed in the UV/TiO_2 system.

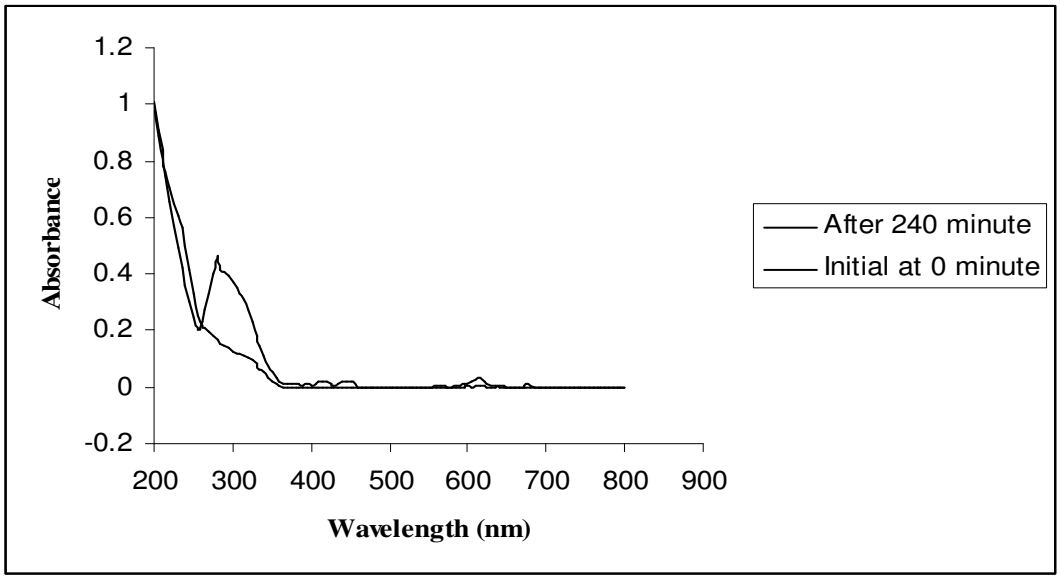

Fig-4.1.9 The full scanning spectrum of PB (25 ppm) in 240 minutes time. [TiO_2] = 500 mg/l, pH=4.0

Several authors have studied the degradation of different dye by the photo catalytic treatment and reported that the complete mineralization and decolorization of dye was observed in UV-Vis. Spectrophotometer (*C.-C. Liu et. al., 2006; S. S. Reddy et. al., 2005; M.A. Behnajady et.al., 2005; J.Bandara et.al., 1996*).

4.2 TREATMENT OF TEXTILE WASTEWATER

Textile wastewater includes a large variety of dyes and chemicals addition that makes the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. The textile mill processes require the input of a wide range of chemicals and dyestuffs, which are generally organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble (*Venceslau et al., 1994, A. A. Kdasl et. al., 2004*).

4.2.1 Characteristics of Wastewater

Wastewater sample was collected from homogenous tank of textile industry. Firstly sample was analyzed for some initial parameters. Textile wastewater was highly

concentrated so sample was diluted to 1:1 with single distilled water before photo catalytic treatment. The values of various wastewater parameters before treatment are shown in Table 4.1

Table 4.1 Characteristics of Wastewater from Textile Industry

S. No.	Parameter	Value
1.	pH	7.49
2.	EC (mS/cm)	3.72
3	Temperature	39
4.	Turbidity (NTU)	142.8
5.	TSS (mg/l)	430
6.	TDS (mg/l)	5770
7.	COD (mg/l)	1250
8.	BOD (mg/l)	496
9.	Color (PCU)	890

These wastewater parameters presented in above table shows that wastewater is highly polluted. So treatment of wastewater is required to facilitate the biological treatment processes and disposal of water into surface water body within the specified disposable limits.

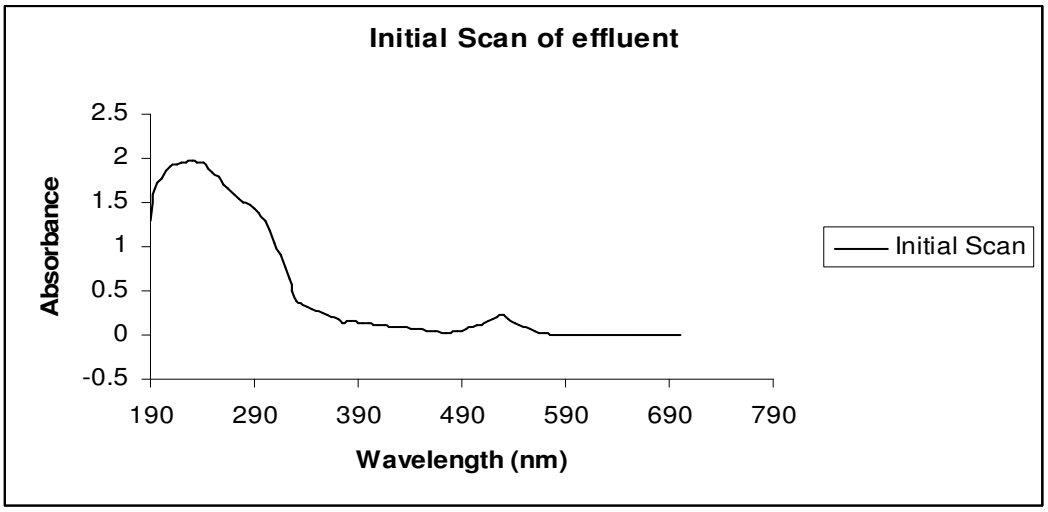

Fig- 4.2.1 Absorption spectra of textile effluent

The raw wastewater has high COD value and it has shown also peaks through absorption spectra. Peak obtained in UV as well as visible region and shows that shows the presence of different organic and chromophoric compounds. Fig-4.2.1 shows UV-Vis absorption spectra of effluent which shows absorption peaks at 379 and 530 nm.

4.2.2 Photocatalytic Treatment

The textile effluent was subjected to photocatalytic treatment and the efficiency of treatment was investigated by altering parameters like pH, catalyst dose, oxidant dose and effect of UV /Solar light.

4.2.3 Influence of Initial pH

Textile industries generate wastewater with a high pH value. Textile wastewaters sample in question has pH of 7.29 which was collected from homogenous tank of effluent treatment plant. pH plays an important role in photocatalytic oxidation processes because pH affects the production of hydroxyl radical which is powerful oxidizing agent. So pH was varied pH from 4.0 to 10 at 2.5 g/l of catalyst dose during experimentation and it was found that with increasing pH there is decrease in degradation rate. The maximum degradation of 86% was observed at pH 4.0 and the final pH after photo catalytic treatment was 7.03 which is suitable for biological treatment as well as discharge of wastewater into the water bodies.

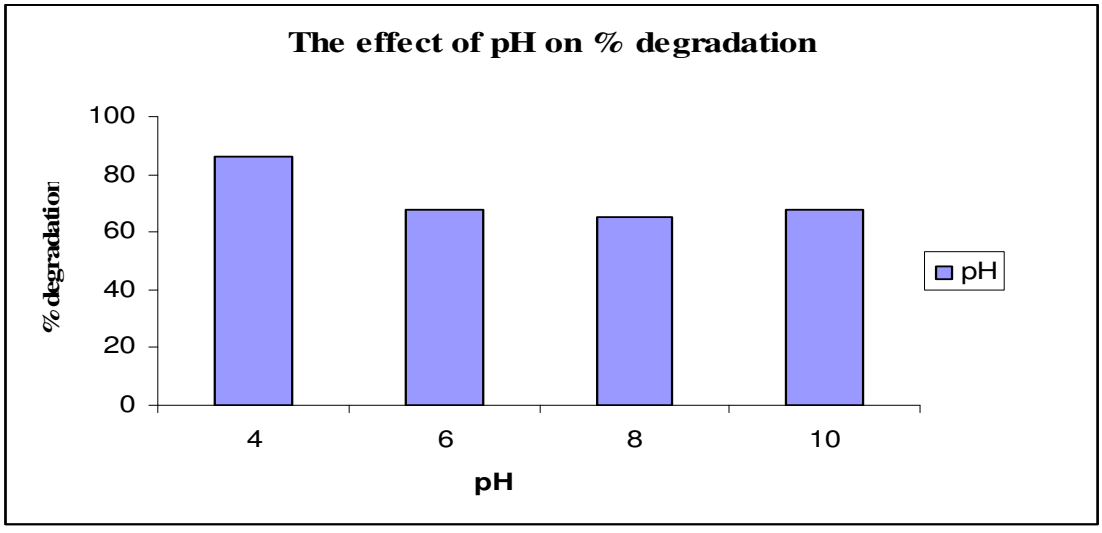

Fig-4.2.3 Effect of initial pH on photocatalytic degradation of textile effluent.

During literature survey it has been found that operating pH of solution significantly affects catalyst activity. *S. S. Reddy and B. Kotaiah (2005)* studied the effect of pH in the range 2-7 for the decolorization of simulated dyeing plant effluent and it is observed that lowering the pH of simulated dyeing plant effluent, significantly improved the color removal efficiency.

4.2.4 Variation of Catalyst (TiO_2) Dose

In order to economize the process at the industrial scale catalyst dose must be optimized. TiO_2 catalyst was used in varying concentration from 1.25 g/l to 5g/l at constant pH 4.0 during the photocatalytic treatment for its optimization. The degradation efficiency was found to first increase upto a catalyst dose of 2.5g/l and then decreases. The maximum degradation (88%) occurred at catalyst concentration 2.5 g/l. Initially the rate of degradation was low at catalyst dose of 2.5g/l but after 2 hrs of exposure the percentage degradation was observed to be maximum as evident from figure. (Fig- 4.2.4) It is also observed that efficiency of photo catalytic process increases with increases in catalyst concentration up to a certain limit and then becomes constant and starts to decrease after certain limit.

The reason for this decrease in efficiency may be due to the clustering of catalyst particles at higher catalyst loading and thus causing a decrease in the number of active site on its free surface. Decrease in opacity and an enhancement of the UV light scattering by TiO_2 particles at higher concentration and thus leading to interruption in the passage of radiation through the wastewater sample in photoreactor may be result in reduced efficiency.

The increased degradation rate that follows with the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are, adsorbed, thus accelerating the process. When all the pollutant molecules are adsorbed on TiO_2 no improvement is achieved by adding more catalyst. Use of higher concentration of catalyst will increase the cost of treatment and decrease the permeability of sunlight.

A. Alinsafi et. al., 2006; S. S. Reddy et. al., 2005; S.K. Dubey, 2006 has reported the similar behavior that as the catalyst concentration increases degradation and

decolorization increases up to a certain limit and adding more catalyst, no further improvement was observed.

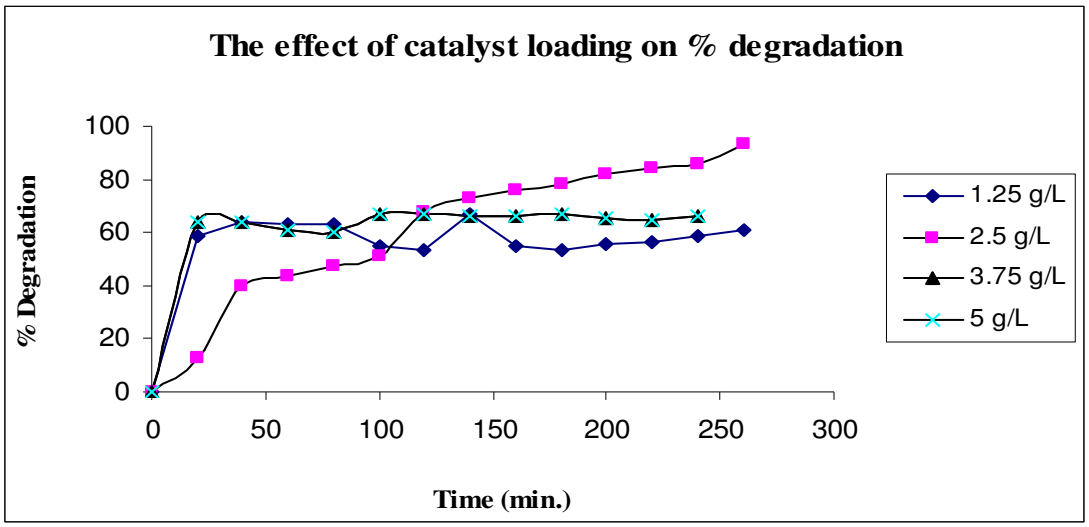

Fig- 4.2.4 Effect of TiO_2 loading on photocatalytic degradation of Textile effluent at 4 pH.

4.2.5 Effect of Oxidant Dose

One possible way to increase the reaction rate is to increase the concentration of ·OH radicals because these species are promoters of photocatalytic degradation. So the concentration of oxidant was varied from 300 mg/l to 1200 mg/l at fixed TiO_2 dose (2.5 g/l) and at constant pH (4.0) during experimentation. Results obtained shows that the degradation rate increases from the 55% to 92%. It is clear from the figure that the maximum percentage degradation 92 % was obtained at 900 mg/l of H_2O_2 dose and it has been taken as optimum amount required for the maximum effective treatment of pollutants. The rate of photocatalytic degradation of wastewater is significantly improved with increase in hydrogen peroxide concentration and reached to a maximum value, beyond which increasing H_2O_2 dose retards the degradation (Fig. 4.2.5). This dual effect of H_2O_2 can be explained by radical reaction mechanisms. By addition of excess H_2O_2, it acts as hydroxyl radical or hole scavenger to form the per hydroxyl radicals ($HO_2^{\bullet}$) which is a much weaker oxidant than hydroxyl radicals.

Therefore, high concentration of hydrogen peroxide inhibited the reaction rate of dye degradation by competing with wastewater for available hydroxyl radicals. A similar observation has been found that an increase in H_2O_2 level enhanced degradation rate up

to an optimum concentration beyond which, inhibition occurs and organic pollutant (*S.K. Dubey, 2006; S. S. Reddy et. al., 2005; M.A.Behnajady et. al., 2005; M. Muruganandham et. al., 2005*).

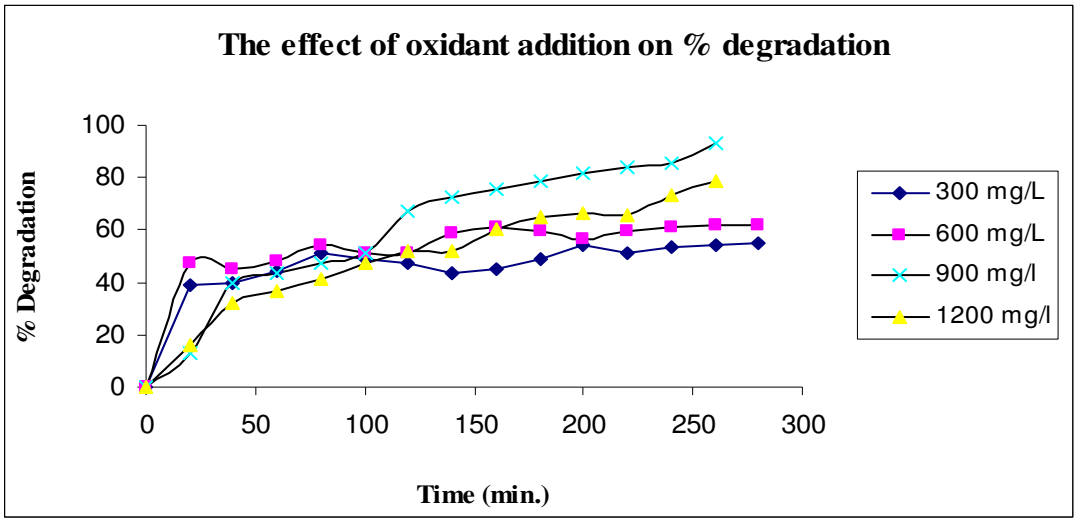

Fig- 4.2.5 Effect of H_2O_2 concentration on photocatalytic degradation of textile effluent. [TiO_2] = 2.5 g/l, pH=4.0.

4.2.6 Degradation with Solar/UV Light

India being a tropical country, there is a free availability of sunlight so for industrial applicability; sunlight is preferred for the wastewater treatment. Hence the aqueous suspensions of TiO_2 containing textile wastewater sample was exposed to solar/UV radiation at optimized parameters. Fig- 4.2.6 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of wastewater sample in the presence of TiO_2 (Degussa P25, 2.5 gL^{-1}) under sunlight and UV light source, respectively. It was found that the extent of degradation of the wastewater sample was more in the presence of UV light source as compared to Solar light.

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.

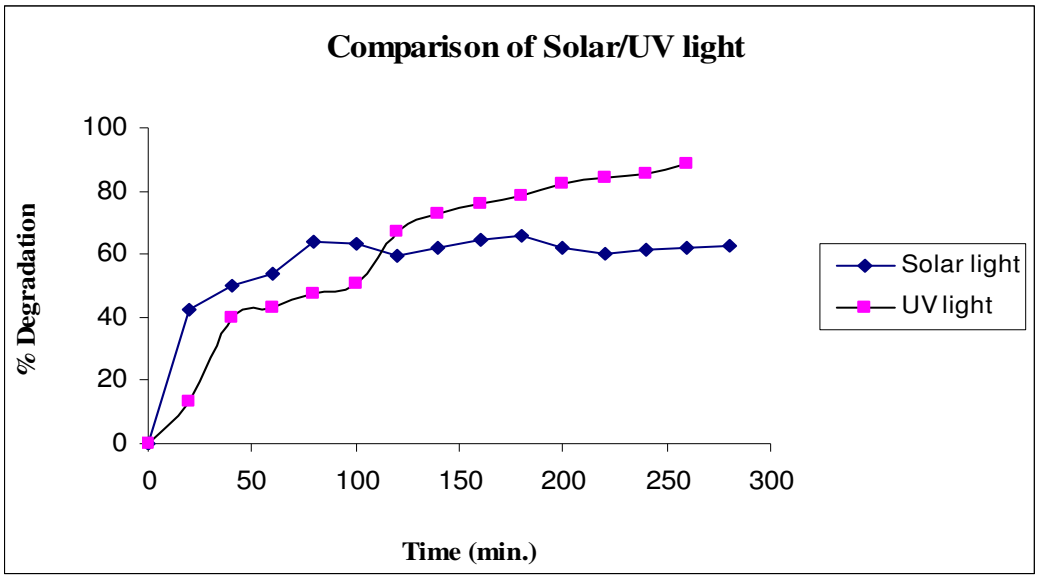

Fig-4.2.6 Effect of UV/Solar light on photocatalytic degradation of textile effluent. [TiO_2] = 2.5 g/l, pH=4.0.

4.2.7 Effluent Characteristics after Photocatalytic Treatment

After the photocatalytic treatment in UV reactor under optimized conditions i.e. at TiO_2 dose of 2.5 g/l and operating pH of 4.0, characterization of the treated wastewater was done. Table- 4.2 showing the parameters analyzed after the 4 hrs of photocatalytic treatment of textile wastewater which shows a major reduction in pollution load. As shown in Fig- 4.2.7 Absorption spectra of the sample after photocatalytic treatment shows no peak in the visible region, indicating the mineralization of several chromophoric compounds previously present in wastewater. This shows that complete degradation of organic compounds in wastewater has occurred. The other parameters like COD, TDS and EC as examined after treatment shows the 74% reduction in COD, 60% TDS reduction after 4 hrs of reaction time. In the presence of solar light COD reduction was found to be 79 %, TDS reduction was 66% after 5 hrs of treatment. Electrical conductivity has been observed to increase.

Table 4.2 Characteristics of Wastewater after Photocatalytic (UV) Treatment Under Optimized Condition

S. No.	Parameter	Value	% Reduction
1.	pH	7.03	--
2.	EC (mS/cm)	4.03	--
3.	Turbidity (NTU)	20.20	86
4.	TSS (mg/l)	105	76
5.	TDS (mg/l)	2370	60
6.	COD (mg/l)	320	74
7.	Color (PCU)	180	80

Table 4.3 Characteristics of Wastewater after Solar Photocatalytic Treatment Under Optimized Condition

S. No.	Parameter	Value	% Reduction
1.	pH	5.61	--
2.	EC (mS/cm)	2.70	--
3.	Turbidity (NTU)	10.78	92
4.	TSS (mg/l)	80	81
5.	TDS (mg/l)	1920	66
6.	COD (mg/l)	260	79
7.	Color (PCU)	202	77

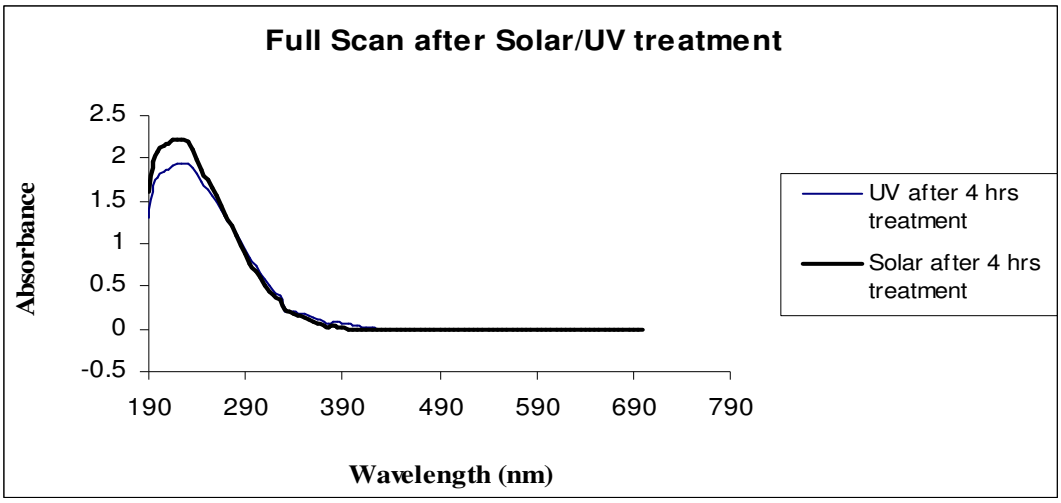

Fig- 4.2.7 Absorption spectra of wastewater after photocatalytic treatment

4.3 Decolorization and Degradation of Textile Wastewater

The wastewater from textile industry was taken for decolorization and degradation study. The properties of wastewater are shown in Table 4.1. Though, it cannot be degraded by conventional biological processes however, the color and COD of the wastewater was significantly reduced by photocatalytic treatment. The complete decolorization of wastewater with TiO_2 catalyst was achieved after 2 hrs irradiation. Chemical oxygen demand (COD) was also reduced to 80 % after 5 hrs of photocatalytic treatment in UV reactor.

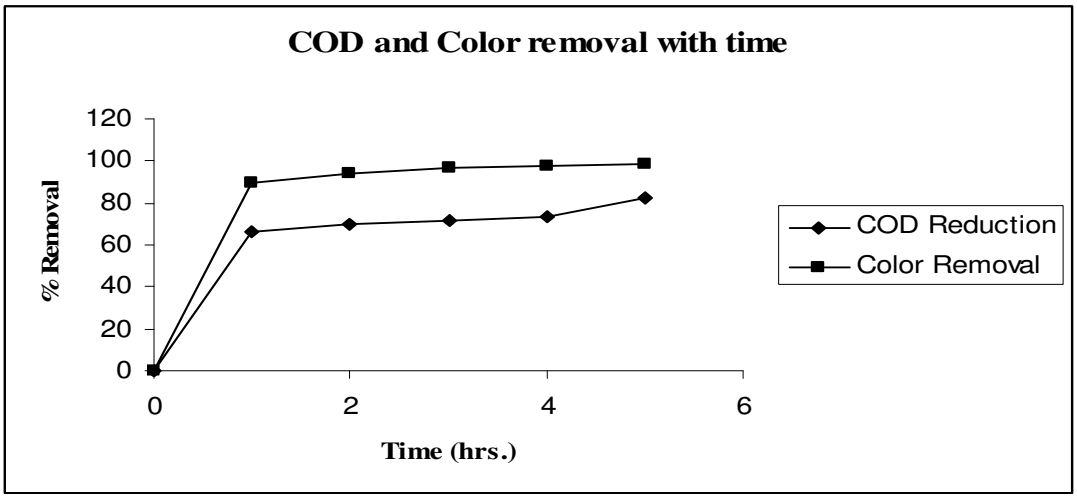

Fig-4.3.1 Percentage color removal and % COD reduction of effluent at different time intervals (pH = 4.0, H_2O_2 = 900 mg/l, TiO_2 = 2.5 g/l)

Fig- 4.3.1 is shows the percentage reduction in COD and Color during photocatalytic treatment of wastewater, clearly indicating that color removal rate was complete and significant reduction in COD was observed for same exposure time.

E.Bizani et.al., 2006; C.C.Liu et.al., 2006;S.S.Reddy et.al.,2005 have studied the effectiveness of photocatalytic treatment for the removal of color and dissolved organic carbon (DOC) reduction from textile wastewater and reported similar indications.

CHAPTER-5

Conclusion

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

Textile wastewater and Procion Blue dye has been successfully degraded in the presence of TiO_2 photocatalyst. In case of dye solution of 25ppm concentration, degradation was found to be 82% and 89 % in UV and solar light respectively at the optimized reaction conditions like pH of 4.0, catalyst dose of 500 mg/l and oxidant concentration of 300 mg/l. Hence, it is deduced that solar light can be effectively used for the degradation and decolorization of dye solution. The diminishing of peaks in the UV and visible region of PB dye during solar/UV photocatalytic treatment shows the complete degradation of organic compounds into simpler end products which results in the complete mineralization of resulting solutions.

Treatment of real textile wastewater has been carried out with variation in parameters like pH, catalyst dose, oxidant concentration and comparison of Solar/UV light. Degradation observed was 92% under optimized conditions i.e. 4.0 pH, catalyst concentration of 2.5 g/l and oxidant dose of 900 mg/l after 260 minutes. In the presence of solar light, 63% degradation has been achieved after 280 minute of reaction time. It has been observed that after 4 hours of photocatalytic treatment, COD reduction of 74%, TDS reduction of 60% and 80% color removal (Co-pt scale) occurs. COD reduction shows in the degradation of organic compounds present in wastewater. Turbidity reduction helps to increase photosynthetic activity in aquatic system and total solids reduction enhances the capability of recycling and reuse of wastewater after treatment.

The important parameters like COD, TSS, TDS, pH and color have been compared with the National Environmental Quality Standards (NEQS) and it is evident from the results that end pH was 7.03 which is neutral, TDS & TSS was 2370 mg/L and

105 mg/L respectively after UV photocatalytic treatment which is well within prescribed standards. If all the conditions remain unchanged, the COD of the treated sample in case of UV and solar photocatalysis was reported to be 320 mg/L and 260 mg/L respectively, so it can be deduced that the COD of resulting effluent in case of solar treatment is much lower than COD reported in UV treatment. Hence, it can be concluded from the observations that solar photocatalysis can be suitably and cost effectively employed for the degradation of real textile effluent with little more retention time.

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