DEGRADATION AND DECOLOURSATION STUDIES OF PAPER MILL EFFLUENTS BY TiO_2 PHOTOCATALYSIS

Thesis submitted in partial fulfillment of the requirements for the award of degree of
Master of Technology
In
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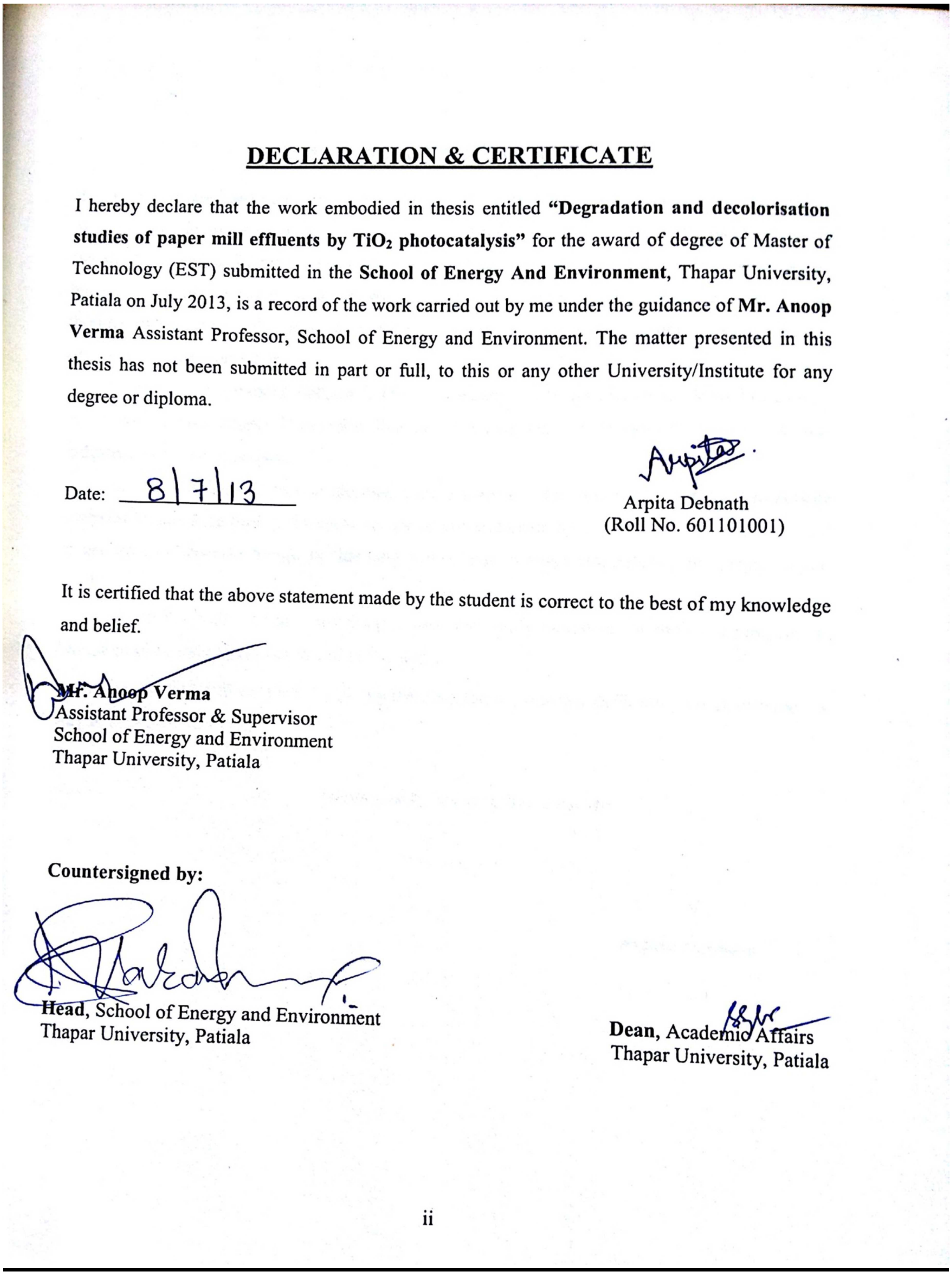

DECLARATION & CERTIFICATE

I hereby declare that the work embodied in thesis entitled **"Degradation and decolorisation studies of paper mill effluents by TiO_2 photocatalysis"** for the award of degree of Master of Technology (EST) submitted in the **School of Energy And Environment,** Thapar University, Patiala on July 2013, is a record of the work carried out by me under the guidance of **Mr. Anoop Verma** Assistant Professor, School of Energy and Environment. 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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It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

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Thank you for making this a reality.

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Abstract

The paper industry has historically been one of the world’s largest consumers of freshwater resources and producers of wastewater discharges. The effluent contains a number of toxic organic compounds that may cause devastating environmental impacts to receiving waters when discharged directly. The scope of this project is to see photocatalysis as a viable treatment option in degrading and mineralizing the recalcitrant organic compounds as well as the possibility of utilizing the solar light spectrum.

The experiments and analysis work is done on actual industrial wastewater. The process optimization like pH, catalyst concentration, oxidant dose, light intensity is carried out to obtain the best result for complete transformation of the toxic organic compounds to benign chemicals. The COD reduction of bleaching effluent observed was 86% and 91% under UV and solar light, respectively (with optimized conditions i.e. 7.5 pH, catalyst concentration of 0.5 gL^{-1} and oxidant dose (H_2O_2) of 2 ml L^{-1}) after 5 hrs of treatment. The biodegradability (BOD_5/COD) of the effluents is improved proposing AOP efficiency as pre-treatment option before biological treatment. Efforts have also been done on the application of AOP for the pre/post-treatment of RO reject water to make it fit for reuse/dilutions in industries. The present study also investigates the efficiency of AOP on color remediation of final ETP effluent. The results of photocatalytic degradation showed that it could be used as pre or post treatment technique for the complete degradation of recalcitrant organic pollutants present in paper mill effluent.

Key words: Advanced oxidation process (AOP), Paper mill effluent, ETP effluent, RO Reject Water, Heterogeneous Photocatalysis and Solar Photocatalysis.

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CHAPTER 1

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1. Introduction

Developed and developing countries are characterized in the society by the production of waste products as standard of living. These countries are facing the problems of biological contamination, heavy metals, intensive nutrients, and organic contamination of water. Phenols, dioxins, pesticides, fertilizers, and detergents are usually non-biodegradable or persistent which effect the environment severely. Moreover, these compounds can transform into potentially dangerous substances during drinking water treatment processes such as chlorination giving chlorocarbons **(Marhaba T. and Washington M., 1998).** Industries involved in the disposal of these types of compounds are mainly pharmaceutical industries, paper and pulp industries, leather-tanning industries, and textile industries. The wastewater from these industries is having problems of color, solids, BOD, COD, pH, high nitrogen content, high sulphur content and is mostly non-biodegradable. Out of all these industries, paper industry is of major concern.

The manufacture of wood pulp is an important method for chemically converting wood into useful products. It is highly important component of the global manufacturing industry in both economic and environmental terms. The mill effluents are mixtures of known and unknown complexes and changing compounds, and because environmental conditions (like DO, pH, temperature) can widely alter the sensitivity of organisms, chances are high that the toxicity will remain important subject for a long time **(Pokhrel D. and Viraraghavan T., 2004).** The effluents from the industry cause slime growth, thermal impacts, scum formation, color problems, and loss of aesthetic beauty in the environment. Among the various sections, the effluents from pulp bleaching are responsible for most of the color, organic matter, and toxicity of the water discharges of this industry **(Kansal S. K. et al., 2008).** The use of chlorine gas and chlorine compounds as bleaching chemicals is known to generate various toxic and bio-refractory chlorinated organic (phenols, resin and fatty acids, dioxins and furans) in the paper mill effluent **(Roy M. et al., 2004).** The conventional effluent treatment processes are not effective for their complete degradation. Hence, treatment with some advanced oxidation processes (AOP's) is needed **(Catalkaya E. C. and Kargi F., 2008).**

Membrane separation processes are becoming quite popular in wastewater treatment and reclamation, since they combine process stability with an excellent effluent quality. The particular advantage is that it operates without heating and thus is energetically usually lower than conventional thermal separation processes **(Einav R. and Lokiec F., 2003).** Nowadays, RO is finding increasing uses in industrial applications because of its effectiveness, compact design, friendly operation, and cost-efficiency. RO is an effective method for handling wastewater but the volume of the reject water (typically as much as 20-50% of the RO feed water volume) is a big issue **(Roberts D.A. et al., 2010).** Even after industries fulfilling the stipulations of the CPCB and SPCBs, discharge of high-TDS reject water by industries in areas where groundwater has high TDS can have serious environmental problems; therefore there is an urgent need for environmentally friendly management options of RO concentrate **(Ismail A.F. et al., 2000)**. RO concentrate could be a valuable and sustainable water resource with available cost-effective treatment schemes. The pollution intensity can be reduced by a proper ETP installed on the premises of the industry to treat the effluent before it is discharged. The discharge of ETP can be used to recover reusable water/other materials and minimizing of polluting substances achieving zero discharge concept.

(Glaze W. and Chapin D., 1987) defined advanced oxidation processes as near ambient temperature and pressure water treatment processes involving the generation of highly reactive radicals (hydroxyl radicals) in sufficient quantity for water purification. They are very promising for remediation of contaminated ground, surface, and wastewater containing non-biodegradable organic pollutants. Hydroxyl radicals are very reactive species attacking most of the organic pollutants, initiating a complex cascade of oxidative reactions leading to mineralization. Acids, Aldehydes, Aromatics, Amines, Alcohols, Dyes and Phenols can be degraded by hydroxyl radicals. Advanced oxidation process (AOP) is complex effluent treatment involving the conversion of organic pollutants to short species and even to their complete mineralization through the generation of highly reactive free radical oxidants **(Al-Kdasi et al., 2005).** Some AOP techniques are: H_2O_2, Fe(II)/Fe(III) with H_2O_2, UV irradiation (direct photolysis), UV/H_2O_2, UV/catalyst/H_2O_2, UV/{Fe(II)/Fe(III) + H_2O_2} and others **(Rodriguesa A.C. et al., 2008).**

Solar photo-catalysis has been found to be efficient in the treatment of some industrial wastewaters **(Neppolian B. et al., 2003).** It consist the use of solar light to generate a highly oxidizing species. Catalysts are needed in the process, being the fenton process and titanium dioxide process, the two most widely employed **(Amat A.M. et al., 2005).** Advanced oxidation process (AOP) employs strong oxidants of H_2O_2 and ozone to degrade organic carbon, especially under the promotion of photo irradiation, catalyst addition (TiO_2, Fe (II), and Fe (III)), thermal input, and ultrasound penetration **(Radwaan and Al-Rasheed, 2005).** The end products of complete oxidation (i.e., mineralization) of organic compounds are carbon dioxide (CO_2) and water (H_2O).

The goal of this study was to analyze the real wastewater and to suggest a method of additional treatment in order to reduce organic pollutants load, which is typically high for the industry. The potential application of optimized photo-assisted oxidation processes using TiO_2 as catalyst, as novel promising alternatives for the reduction of total dissolved solids (TDS) and color from RO rejects water and treated effluent, respectively. Photocatalysis was suggested as the method of advanced treatment for bleaching effluent and comparison of the efficiency of TiO_2 photocatalytic reactions with and without addition of H_2O_2. The application of fixed bed photocatalysis to treat waste water is also studied. Considerable attention has been focused on the possibility of combining heterogeneous catalysis with solar technologies to achieve the mineralization of toxins present in wastewater.

CHAPTER 2

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2. Objectives

The main objectives of this study are:

- To investigate the advanced treatment of bleaching effluent (BE) using photocatalytic process and study the effect of various parameters such as concentration of catalyst, pH, $H_2O_{2,}$ reuse of catalyst on efficiency of degradation rate.
- To study the viability of treatment of RO reject water (RRW) by photocatalytic process.
- To investigate the decolourization rate of treated effluent (TE) by advanced oxidation process.

CHAPTER 3

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3. Literature Review

Both small-scale and large-scale industrial activities produce wastewater contaminated by a variety of organic pollutants. Almost all the rivers of India, at least in certain stretches, are heavily polluted by the discharge of industrial wastewater. Most components of industrial effluents are toxic to ecological systems even at low concentrations, and many are non-biodegradable. A large number of inorganic chemicals pollute surface water from sources such as industrial plants, mines, oil drilling, and municipal storm water.

3.1. Overview of Pulp and Paper Industry

Pulp and paper mills are a major source of industrial pollution worldwide. The pulping and bleaching steps generate most of the liquid, solid, and gaseous wastes **(Smook G.A., 1992).** These are energy intensive and typically consume huge volumes of fresh water and large quantities of chemicals such as sodium carbonate, sodium hydroxide, sodium sulfide, bisulfites, elemental chlorine or chlorine dioxide, hydrochloric acid, calcium oxide and so on.

The paper and pulp production is based on the use of raw material such as wood, but also on the consumption of large-scale chemicals (**Singh P. and Thakur I.S., 2006).** The usual substrate for paper production is the slurry of cellulose in water. The source of cellulose is the wood and agricultural waste (wheat straw, sarkanda), imported wood and waste paper. The wood contains two additional components: lignin and hemicelluloses **(Grimvall A, 1991).** Whereas cellulose is a polymer of glucose units, the molecules of the monomer n-propyl-benzene, bound by either -C-O-C- and -C-C- bonds compose lignin molecules. Because of the high content of benzene rings in its molecules, lignin is easily oxidized and darkens. Hemicellulose is composed by polymers with lower molecular mass, being intermediates of the biosynthesis of cellulose.

3.1.1. Process Description

The paper manufacturing process has been divided in the following stages- Wood Preparation, Pulping, Bleaching, Chemical Recovery, and Paper Making

- Wood Preparation

This step involves breaking wood down into small pieces suitable for subsequent pulping operations. Major wood preparation processes are debarking and chipping.

- Pulping

  Pulp making has as an aim digesting the raw material into its fibrous components via chemical, mechanical or combinations of different methods. The Kraft process, which is the most common, uses sodium hydroxide and sodium sulfite solution. The sulfite process uses a mixture of sulfurous acid and bisulfate iron (typically from sodium sulfite). Chemical methods lead to release of cellulose fibers by destroying the chemical bonds in the glue-like lignin, which bonds fibers together. It is the most water-consuming stage, i.e. for a large-scale pulp mills operating by the kraft method, it takes approximately 16 million cubic meters daily, or about 50 cubic meters/ton pulp.

- Bleaching

  Bleaching whitens pulps for the manufacture of writing, printing, and decorative papers. The process alters or removes the lignin attached to the wood fiber. Chemical pulps are bleached through the use of alternating treatments of oxidizing agents and alkali solutions. The kraft process produces a darker pulp that requires more bleaching. Mechanical pulps are treated with hydrogen peroxide or sodium hydrosulfite to reduce the light absorption of the lignin rather than remove it.

- Chemical Recovery

  Chemical recovery regenerates the spent chemicals used in kraft chemical pulping. Chemical pulping produces a waste stream of inorganic chemicals and wood residues known as black liquor. The black liquor is concentrated in evaporators and then incinerated in recovery furnaces, many of which are connected to steam-turbine cogeneration systems. The wood residues provide the fuel and the chemicals are separated as smelt which is then treated to produce sodium hydroxide. Sodium sulfide is also recovered.

- Papermaking

  Papermaking consists of preparation, forming, pressing and drying. Preparation and drying are the most energy intensive processes. During preparation, the pulp is made more flexible through beating, a mechanical pounding and squeezing process. Pigments, dyes, filler materials and sizing materials are added at this stage.

3.1.2. Wastewater Characteristics

Different pulping processes utilize different amount of water and all of these processes are water intensive. The wastewater quality generated from pulping and bleaching is significantly distinctive because of the process and chemical types **(Billings and Dehaas, 1971)**. Wood preparation, pulping, pulp washing, screening, washing, bleaching, paper machine and coating operations are the most important pollution sources among various process stages **(Cecen F. et al., 1992).** The wastewaters generated from pulping process consist of various wooden compounds such as carbohydrate, lignin and extractives and the treatment of these wastewaters biologically is difficult. Also, some toxic compounds such as resin acids, unsaturated fatty acids, diterpene alcohols, chlorinated resin acids, juvaniones and others can exist in the wastewaters subjecting to the process **(Pokhrel D. and Viraraghavan T., 2004).** The bleaching wastewaters are not higher in strength than pulping process wastewater, however they include toxic components. The most important reaction in the bleaching step is oxidation of chlorine and the main problem about the bleaching wastewater content is chlorinated organic compounds or AOX **(Sumathi S. and Hung Y. T., 2006).** The color of treated effluent is not aesthetically acceptable. The standard of waste discharge quality is shown in table 3.1

S.No.	**Parameter**	**Paper mill effluent**	**ETP effluent**
1.	pH	6.0-9.0	5.5-9.0
2.	COD (mg l^{-1})	250	250
3.	BOD_5 (mg l^{-1})	100	30
4.	BOD/COD ratio	0.4	0.12
5.	Conductivity (μmho/cm)	1200	1000
7.	TDS (mg l^{-1})	2100	2100
8.	TSS (mg l^{-1})	500	100
9.	Chloride (mg l^{-1})	600	1
10.	Fluoride (mg l^{-1})	10	2
11.	Phosphorous (mg l^{-1})	10	2
12.	Sulphate (mg l^{-1})	2	1000
13.	Color (Pt-Co units)	50-2500	50-1000

Table 3.1 Standards of effluent (Devi, N. L., et al., 2011)

3.1.3. Environmental Impacts of Bleaching Effluent

Pulp and paper industry is the sixth largest polluter (after oil, cement, leather, textile, and steel industries) discharging a variety of liquid, gaseous and solid wastes into the environment. The effluent released by bleaching and pulping are amongst the most polluter and are characterized by parameters unique to these wastes causing considerable damage to the receiving waters if discharged untreated since they have a high biochemical oxygen demand (BOD), chemical oxygen demand (COD), chlorinated compounds (measured as AOX), suspended solids (mainly fibers), tannins, fatty acids, resin acids, lignin and its derivatives, sulfur and sulfur compounds, etc. **(Mishra et al., 2009).** The undiluted effluents are toxic to aquatic organisms and exhibit strong mutagenic effect.

Furthermore, some compounds in the effluents are resistant to biodegradation and can bioaccumulate in the aquatic food chain. Dark brown coloration of the receiving water bodies result in reduced penetration of light, thereby affecting benthic growth and habitat. The color responsible for causing aesthetic problems is attributable to lignin and its degradation products **(Ali M. and Sreekrishnan T.R., 2001).** High content of organic matter, which contributes to the biological oxygen demand (BOD) and depletion of dissolved oxygen in the receiving ecosystems. While some of these pollutants are naturally occurring wood extractives (tannins, resin acids, lignin), others are xenobiotic compounds (chlorinated lignins, resin acids and phenols, dioxins, furans). Some of the pollutants such as polychlorinated dibenzodioxins and dibenzofurans (dioxins and furans), are recalcitrant to degradation and tend to persist in nature.

In order to achieve different levels of contaminant removal, individual waste-water treatment procedures are combined into a variety of systems, classified as primary, secondary, and tertiary waste-water treatment (**Ollis D. F. et al., 1989).** The use of conventional water and wastewater treatment processes become increasingly challenged with the identification of more and more contaminants, rapid growth of population, industrial activities, and diminishing availability of water resources. The major drawback of conventional methods is not able to treat toxic, non biodegradable organic pollutants (**Mills A. and Davis R.H., 1993)** so to meet the challenge of keeping progress in wastewater pollution abatement ahead of population growth, changes in industrial processes and technological developments, advance oxidation techniques have emerged in the past few years, in particularly for industrial waste water.

3.2. Membrane separation technology

Membrane separation processes are becoming quite popular in wastewater treatment and reclamation, since they combine process stability with an excellent effluent quality. Suspended and colloidal solids, as well as pathogens can be removed from the membrane bioreactor (MBR) (microfiltration, ultrafiltration), while the reverse osmosis (RO) membrane removes ions and organic matter **(Ismail and Yuliwati, 2000).** The particular advantage of membrane separation processes is that it operates without heating and thus is energetically usually lower than conventional thermal separation processes (distillation, sublimation or crystallization). This separation process is purely physical and, the use of both fractions (permeate and retentate) is possible. The growing demand for fresh water is partially satisfied by desalination plants that increasingly use membrane technologies and among them reverse osmosis to produce purified water. Reverse osmosis was introduced during the 1950s, it has been most commonly been used for purifying water and removing salts, dissolved solids and other impurities in order to improve the color, taste or properties of the fluid for portability. Nowadays, RO is finding increasing uses in industrial applications (mining industries, production of potable water and more recently in tertiary wastewater treatment) because of its effectiveness, compact design, friendly operation, and cost-efficiency.

3.2.1. Value addition to RO reject water

The inorganic and organic contents in the RO concentrate must be reduced to an acceptable level by potential treatments such as solar evaporation (evaporation ponds), wind aided intensified evaporation, membrane distillation, forward osmosis, electrodialysis **(Lez et al., 2011),** vacuum membrane distillation **(Liu et al., 2008),** electro-oxidation **(Pe´rez et al., 2010),** crystallization, capacitive deionization **(Lee et al., 2009).** An alternative treatment methodology is to employ AOPs. Fenton process is one of the most common AOPs used for wastewater treatment because it is usually very efficient and implies a lower economical cost than others but it is limited by the final production of iron sludge, which requires ultimate disposal **(Hermosilla et al., 2012).** The method that is adopted for the wastewater treatment is heterogeneous photocatalysis with TiO_2 as a catalyst is a technology with many advantages including the possible use of solar radiation. The catalyst is of low cost, commercially available, non-toxic and photochemically stable. Coupling AOPs with other treatment technologies such as activated carbon adsorption, coagulation, sonolysis, ozonation would be effective alternatives to achieve high organics removal efficiency **(Dialynas et al., 2008).** Another mechanism is to use reject water for dilution with power plant cooling waters (**Einav and Lokiec, 2003)** or diluted with natural seawater or municipal wastewaters to reduce salinity prior to discharge **(Roberts et al., 2010).**

3.3. Treatment Technology

3.3.1. Photocatalysis in water treatment

Destruction of chromophoric and non-chromophoric pollutants in pulp and paper effluents may be achieved by advanced oxidation methods such as photocatalysis **(Toor A. P. et al., 2006)**, photo-oxidation using hydrogen peroxide (H_2O_2)/UV or ozone (O_3)/UV systems, fenton-type reactions, wet oxidation, and by employing strong oxidants such as ozone**.** The photocatalytic detoxification has been discussed as an alternative method for cleaning up of polluted water in the scientific literature since 1976 (**Carey J. H. et al., 1976).** The presence of harmful organic compounds in water supplies and in the discharge of wastewater from chemical industries, power plants, landfills, and agricultural sources is a topic of global concern. Heterogeneous photocatalysis on metal oxide semiconductor particles is an advanced oxidation technology (AOT), which has been shown to be an effective means of removing organic pollutants from water streams. Compared with traditional oxidation processes, heterogeneous photocatalysis has the following advantages (**Hoffmann M. R. et al., 1995).**

- It utilizes low-energy ultraviolet light with semiconductors acting as photocatalyst and leads to complete mineralization of pollutants to environmentally harmless compounds.
- The photocatalytic reactions allow thermodynamically unfavorable reactions to occur and allow destruction of non-biodegradable refractory contaminants.
- While catalytic processes normally require high temperature or high pressure, Photocatalytic oxidation is a promising technique for many purposes due to its ability to operate at or slightly above ambient conditions.

However, the rate of the photocatalytic reaction is determined by the illuminated surface area of photo catalysts, light irradiance, reactants adsorption rate, and the properties of photo catalysts. Generally, the rate is not significantly great due to the low photo efficiency. Thus commercialization of photocatalytic processes is still in its infancy. There are mainly two types of configurations as far as the catalyst is concerned - either as a slurry of titania in suspension or immobilized on inert surfaces. Slurry reactors necessitate downstream separation and recycle of the catalyst and are inefficient and difficult to scale up. Therefore, immobilized reactors are preferred.

3.3.2. Mechanism of AOP

Advanced oxidation processes (AOP's), uniting together high output ultraviolet technologies, in conjunction with hydrogen peroxide and catalyst are successfully used to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without producing additional hazardous by-products or sludge which require further handling (**Gogate P.R. and Pandit A.B., 2004)**. Advanced oxidation processes involve the generation of hydroxyl ($^{\cdot}OH$) radicals which oxidize the pollutants. After fluorine, the hydroxyl radical is the second strongest known oxidant having an oxidation potential of 2.8 eV. It is able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions as shown in Eq1 and Eq 2.

$$\bullet OH + RH \rightarrow R\bullet + H_2O \qquad \text{(Eq 1.)}$$

$$R\bullet + O_2 \rightarrow RO_2\bullet \rightarrow \text{Products and } CO_2 \qquad \text{(Eq 2.)}$$

Different combinations of homogenous and heterogeneous methods which involve the generation of free radicals are, (i) photochemical irradiation with ultraviolet light (coupled with powerful oxidizing agents like ozone, hydrogen peroxide and /or a semiconductor), (ii) Fenton and Photo-Fenton catalytic processes (iii) Electron Beam Irradiation technique and (iv) Sonolysis. (**Balchioglu A. et al., 2003).**

The catalysts absorb at wavelengths of solar spectrum like hydrogen peroxide and ozone. Since hydroxyl radical generation is the key step in oxidation, oxidation potential of common oxidants are important to be known **(Toor A.P. et al., 2005).** All these processes use UV range for degradation. The UV spectrum is arbitrarily divided into three bands: UV-A (315 to 400 nm), UV-B (280 to 315nm) and UV-C (100 to 280 nm). Of these bands UV-A and UV-C are generally used in environmental applications. UV-A radiations are referred to as long wavelength radiations or black light and UV-C are referred to as short wave radiations.

Advanced oxidation processes can be broadly classified **(Wu S., 1999)** into the following groups:

1. Homogeneous photocatalysis
2. Heterogeneous photocatalysis

3.3.2.1. Homogeneous photocatalysis

The applications of homogeneous photo degradation (single-phase system) to treat contaminated water, involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The major oxidants used are:

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

Many of the AOP's utilize the chemical, hydrogen peroxide. The oxidizing strength of hydrogen peroxide alone is relatively weak, but the addition of UV light enhances the rate and strength of oxidation through production of increased amounts of hydroxyl radicals. Hydrogen peroxide may also be used to enhance other AOP’s if added in low concentrations, as the molecule easily splits into two hydroxyl radicals.

3.3.2.2. Heterogeneous photocatalysis

Heterogeneous photocatalytic process consists of utilizing the near UV radiation to photo-excite a semiconductor catalyst in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radicals or free holes, are generated as shown in figure 3.1. Using photocatalysis, organic pollutants can be completely mineralized reacting with the oxidizers to form CO_2, water and dilute concentration of simple mineral acids **(Mohamed O.S., 2002).** The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of solar spectrum ($\lambda < 380nm$) what transforms it into a good option to be used.

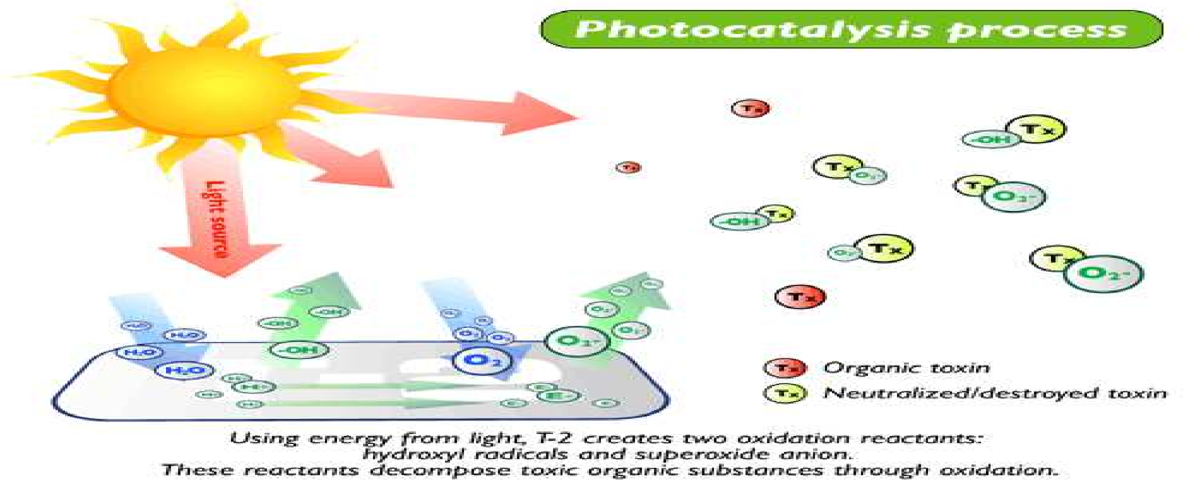

Figure 3.1 Schematic representation of the processes occurring in and on semiconductor particles during the Photocatalytic mineralization of organic molecules by oxygen.

The semiconductor may be in the form of a powder suspended in the water or fixed on a support. Among the various semiconductors, TiO_2 has proven to be the most suitable for widespread environmental applications. ZnO also seems to be a suitable photocatalyst but it dissolves in acidic solutions and therefore, cannot be used for technical applications. Other semiconductor particles (e.g. CdS) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates, but unfortunately, such catalysts are degraded during the repeated catalytic cycles usually involved in heterogeneous photocatalysis **(Botía D. C. et al., 2012).**

This semiconductor exists in three crystalline forms: anatase, rutile, and brookite. Anatase and rutile are the most common forms and the former is the most effective in wastewater treatment. The band gap energies are approximately 3.2 eV for anatase and 3.0 eV for rutile but the driving force for oxidative processes are similar. Anatase is thermodynamically less stable than rutile, but its formation is kinetically favored at lower temperature (<600^{o}C), which could explain its higher surface area and its higher surface density of active sites for adsorption and catalysis **(Parilti N. B. and Akten D., 2011).** Furthermore, TiO_2 is of special interest since it can use natural (solar) UV radiation. This is because TiO_2 has an appropriate energetic separation between its valence and conduction bands, which can be surpassed by the energy of a solar photon.

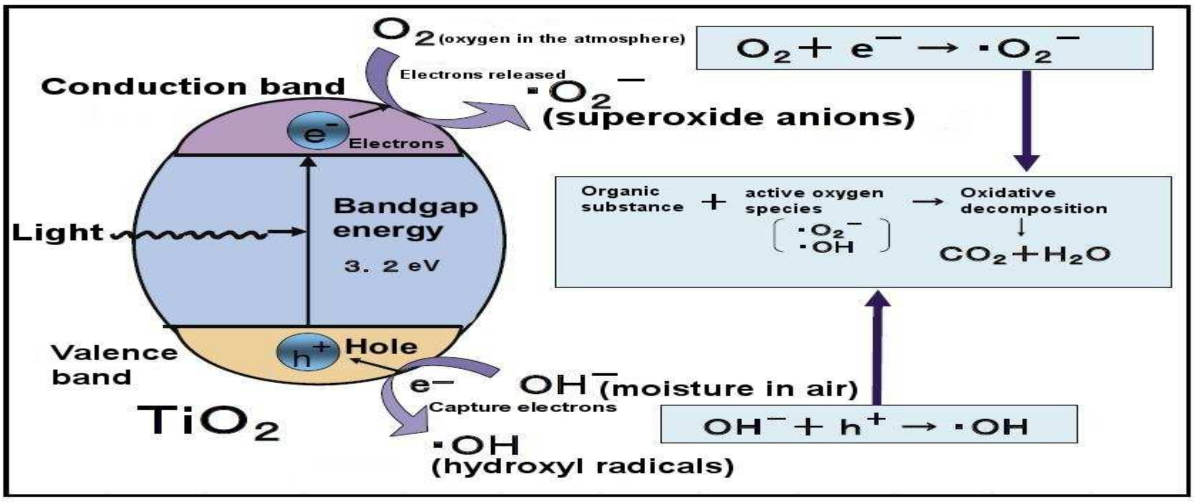

Figure 3.2 Working principle of TiO_2 catalyst.

The primary photocatalytic mechanism **(Andreozzi et al., 1999)** is believed to proceed as follows:

$$TiO_2 + hv \longrightarrow e^-_{CB} + h^+_{VB}$$

$$h^+_{VB} + H_2O \longrightarrow {}^{\bullet}OH + H^+$$

$$e^-_{CB} + O_2 \longrightarrow O_2^{\bullet -}$$

$$2O_2^{\bullet -} + 2H_2O \longrightarrow H_2O_2 + 2OH^- + O_2$$

$$H_2O_2 + e^-_{CB} \longrightarrow OH^- + {}^{\bullet}OH$$

In solids, the electrons occupy energy bands as a consequence of the extended bonding network. In a semiconductor, the highest occupied and lowest unoccupied energy bands are separated by a band gap, a region devoid of energy levels. Activation of semiconductor photocatalyst is achieved through the absorption of a photon of ultraviolet band gap energy which results in promotion of an electron (e^{-1}) from the valence band (VB) into the conduction band (CB) with the generation of hole in the valence band as shown in the figure 3.2**.** The resulting hole is an oxidizing agent and the electron is a reducing agent. In the generally accepted mechanism for the photocatalytic process, the hole can react with water to generate the hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution. This creates the reactive radicals responsible for the removal of hazardous components from the water.

3.3.3. Solar Photocatalyst

In the near future, advanced oxidation processes (AOPs) may become the most widely used water treatment technologies for organic pollutants not treatable by conventional technologies due to the high chemical stability and/or low biodegradability of such pollutants **(Gogate P. R.et al., 2004; Pera-Titus M. et al., 2004).** The main disadvantage of AOPs is their high cost. The use of AOPs for wastewater treatment has been studied extensively, but generation of UV radiation by lamps or ozone production is expensive **(Muñoz I. et al., 2005).** Therefore, research is focusing more and more on those AOPs, which can be driven by solar irradiation, i.e., light with a wavelength longer than 300 nm.

3.4. Photocatalysis in paper mill wastewater treatment

In general the AOPs when applied in a right place, give a good opportunity to reduce the contaminants concentration. That is why they are called the water treatment processes of the 21st century. At the same time the knowledge about the exact mechanisms of AOPs is still incomplete. AOPs are important tools for environmental technology and they must be placed on sounder scientific and engineering basis. **(B. Bayarri et al., 2007)** investigated photocatalysis can be a useful tool in the treatment of same recalcitrant and toxic pollutants. However some problems arise in the modeling of photocatalytic systems, most of them related to the radiation field. In this work, some methods are presented which can be powerful tools in the evaluation of the radiation absorbed by the photocatalyst, which is the energy really useful in promoting the photocatalytic process. All methods are based on actinometric procedures carried out in different experimental conditions and using different photoreactors. Different advanced oxidation processes (AOPs) had been applied to remove the organic carbon content of a paper mill effluent originating from the kraft pulp bleaching process resulted in a considerable decrease in dissolved organic carbon (DOC) content with variable treatment efficiencies depending upon the nature/type of the applied AOP **(Muñoz I. et al., 2006).** A study on the photocatalytic degradation of eight azo dyes was conducted in basic medium, studying the influence of various amounts of TiO_2 and different light sources, a medium pressure (400 W) and a low pressure (16 W) Hg vapour lamps and lamps for household purposes. The experiments were monitored by UV-VIS absorption and the degree of mineralisation was followed by COD variation. Decolouration extents observed are related to dye structure. The photocatalytic degradation of dyes in solution, containing titanium dioxide, is feasible using UV light, but expensive due to the light source needed **(Gonqalves et al., 1999).**

Another studied the photocatalytic degradation of three commercial textile dyes with different structure using TiO_2 (Degussa P25) photocatalyst in aqueous solution under solar irradiation. Experiments were conducted to optimize various parameters viz. amount of catalyst, concentration of dye, pH and solar light intensity. Degradation of all the dyes were examined by using chemical oxygen demand (COD) method. The experimental results indicate that TiO_2 (Degussa P25) is the best catalyst in comparison with other commercial photocatalysts such as, TiO_2 (Merck), ZnO, ZrO_2, WO_3 and CdS because of its multiphase purity, large band gap and non-corrosive nature. Further the same catalyst can be used for a number of cycles which will reduce the cost of operation **(Neppolian et al., 2002).** The degradation of phenolic and polyphenolic compounds present in a bleaching ECF effluent for different advanced oxidation systems was described with $O_2/ZnO/UV$, $O_2/TiO_2/UV$. The homogeneous systems O_3 and O_3/UV also degrade the organic matter but at a lower extent considering the same time of reaction. Reactions were monitored by color changes, pH, COD and BOD (**Mansilla H.D. et al., 1997).**

The advanced photocatalytic oxidation of the pulp and paper industry effluent (primary clarified and biotreated) had been studied and results shows that organic load was removed and BOD/COD ratio of the effluents was also improved after treatment with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes, respectively **(Kumar P. et al., 2011).** Another study investigated the degradation of elemental chlorine free (ECF) bleaching effluents by two catalytic systems: $O_2/TiO_2/UV$ and $O_2/ZnO/UV$ at different periods of irradiation. The process efficiency was increased by color reduction, UV/Vis analysis, total phenol content and molecular weight distribution of the untreated and treated effluent **(Mattos L.R. and Silva F.T., 2002).** In one study, the biological treatability of sulfate pulp bleaching effluents was enhanced with TiO_2 photo catalyzed oxidation characteristics **(Balcioğlu I.A. and Çeçen F., 1999).** The laboratory study aimed at improving the treatability of bleaching effluents from local pulp and paper mills using individual physico-chemical treatments like chemical precipitation, electrochemical treatment and advanced oxidation processes such as ultrasonic irradiation in combination with fenton-like oxidation (Fe^{3+}/H_2O_2) or photo-fenton degradation ($Fe^{2+}/H_2O_2/UV$). The effects of operating parameters such as pH and oxidant's dose on the removal of organic compounds were investigated in terms of COD removal (**Hoffmann M. R. et al., 1995).**

An investigation of bleaching plant effluent is done using TiO_2 and effects of COD values, UV intensity, aperture-to-volume ratio was studied **(Toor A.P., 2007).** Pulp mill effluent containing toxic chemicals was treated by different advanced oxidation processes (AOPs) consisting of treatments by hydrogen peroxide, fenton's reagent (H_2O_2/Fe^{2+}), UV, UV/H_2O_2, photo-Fenton ($UV/H_2O_2/Fe^{2+}$), ozonation and peroxone (ozone/H_2O_2) in laboratory-scale Almost every method used resulted in some degree of colour and COD removal **(Catalkaya E.C. and Kargi F., 2006).** A study showed solar degradation of effluents in board paper industries using different photo-catalysts: fenton reagent and TiO_2 **(Amat A.M. et al., 2005).** A study stated that paper industry is being forced to adopt a zero liquid effluent policy and so reverse osmosis (RO) systems are being assessed as the final step of effluent treatment. The treatment can be devised by several promising advanced oxidation processes (AOPs) – conventional Fenton, photo-Fenton and photocatalysis – was optimized considering the effect and interaction of reaction parameters. Although TiO_2-photocatalysis showed the least efficient and most expensive figures, it improved the biodegradability of the retentate, so its combination with a final biological step almost achieved the total removal of the COD (**Hermosilla et al., 2012**). The solar photocatalytic degradation of paper mill wastewater had been studied over synthesized nano TiO_2 showing that prepared TiO_2 can be employed as an effective photocatalyst for the removal of COD from the wastewater but in optimized conditions **(Ghaly M.Y. et al., 2011).** A study evaluates the sequencing of photocatalysis with the biological treatment is efficient and technically viable process for the complete mineralization of the effluents from chlorination and first alkaline extraction stages of soda pulp bleaching in agro-residue-based pulp and paper mill **(Dhir A. et al., 2012).**

CHAPTER 4

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4. Materials and methods

Raw effluents were collected from paper industry, Punjab. The sample was checked for some initial parameters and then treatment was done.

4.1. Reagents and chemicals Used

The photocatalyst was TiO_2 P-25 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, procured from Degussa company, India branch, Bombay). Hydrogen Peroxide (Ranbaxy laboratories) was used as an oxidant. 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 concentrate sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and ferroin indicator. For determination of BOD, phosphate buffer, calcium chloride, ferric chloride, magnesium sulfate, managenous sulphate, potassium iodide, sulphuric acid, sodium thiosulphate and starch as indicator were used. For sulphate determination, barium chloride was used and for chloride determination, silver nitrate and K_2CrO_4 indicator were used. For phosphorous determination, stannous chloride solution, ammonium molybdate, standard phosphorous solution were used and for fluoride determination, SPANDS solution, standard fluoride solution, zirconyl acid reagent were used (Standard Method).

In all experiments distilled water was used. Different normality of (0.1N H_2SO_4 and 0.1 N NaOH) was used for adjustment of pH of sample.

4.2. Instrument Used

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 0.1 N NaOH and 0.1 N HCl. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

Electrical conductivity meter

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

Turbidity meter

Turbidity of the samples was measured by using Hatch Radio turbidometer as per STANDARD METHODS for the examination of water and wastewater 1999 (20th edition).

COD digester

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

Spectrophotometer

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

Magnetic stirrer

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

Air sparger

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

Radiometer

Solar/UV Intensity was measured hourly during experimental days with Eppley (model no. 33013) radiometer. Figure 4.1 is a picture of the same radiometer.

Figure 4.1 Eppley Radiometer

Filtration

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

UV chamber details

Photo catalytic treatment of effluent was performed in batch experiments in UV chamber rectangular in shape having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of wood. Roof of the reactor was fitted with seven UV tubes (36 Watt each) in parallel.

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.

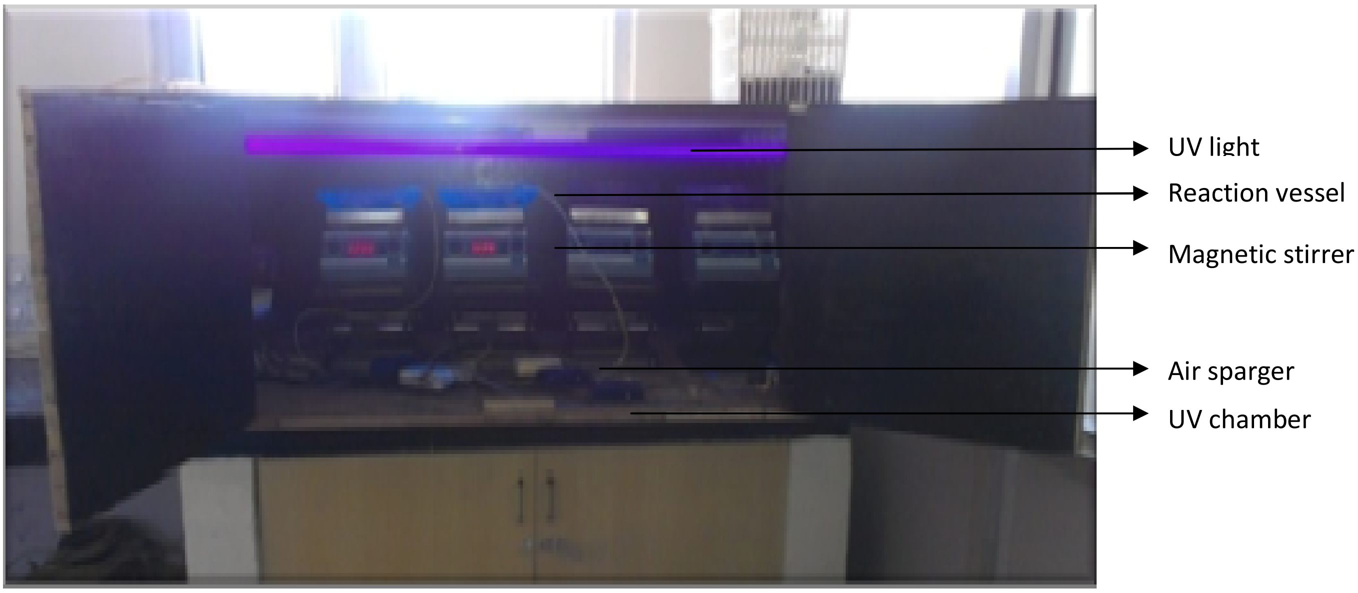

Figure 4.2 Photo reactor at lab scale during photocatalytic treatment

Reaction vessel

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

Figure 4.3 Reaction Vessel under (a) UV light (b) Solar light

Glass plate photoreactor

For fixed bed photocatalysis, the coated glass plate (i.e.glass plate dipped in 5% aqueous solution of catalyst for overnight and then dried at room temperature) was kept vertically inclined at an adjustable angle of 22° from the ground. Effluent samples were recirculated at the flow rate of

0.5 lt/min, through a fish aquarium pump with the help of rubber tubing and collected in a covered bucket and re-circulated again **(Jayant S., 2012)**

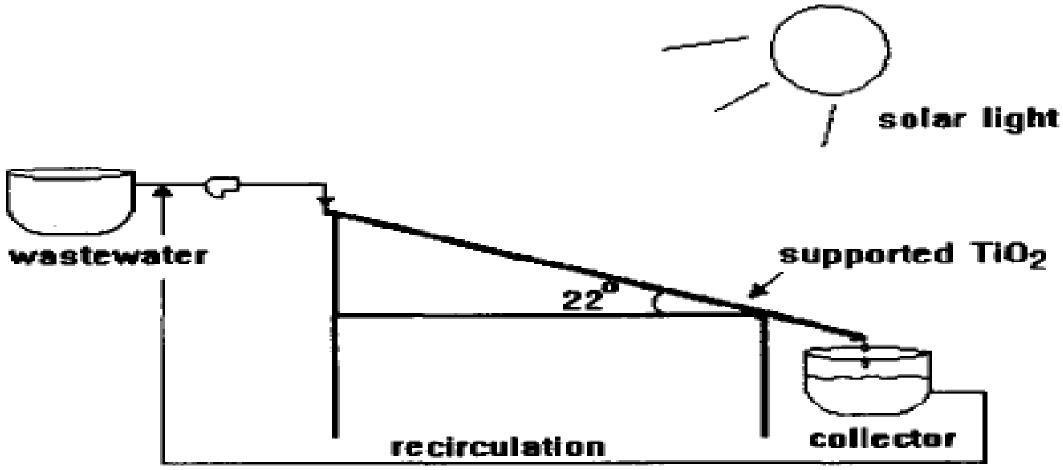

Figure 4.4 Schematic view of TiO_2 fixed-bed solar reactor (Raquel F.P. et al., 1996)

4.3. METHODS

4.3.1. Collection and storage of wastewater

Sample was collected from paper industry. Sampling vessel was cleaned and rinsed carefully with distilled water and then washed with sample during sample collection. Then BE was stored in cold store at 4°C within 3 to 4 hrs of collection.

4.3.2. Characterization of wastewater sample

Wastewater sample was analyzed for the COD, BOD, TDS, TSS, Turbidity, pH, EC, 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 1999 (20th edition). Reagents used for the present investigation were of AR Grade and single distilled water was used throughout the study.

4.3.3. Preparation of solution

a) 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 effluent, add 10 ml in 1 L of sample or 1 ml of diluted peroxide solution in 100 ml of solution.

4.4. Techniques

Estimation of COD

COD was estimated as per the standard method No. 5220 C, page No.5-14 from STANDARD METHODS for the examination of water and wastewater, 1999 (20th edition).

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, 1999(20th edition). BOD was estimated by BOD bottle method.

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.

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.

Analysis of sulphates

Sulphates were estimated as per the standards methods No.4500, page No. 4-189 of STANDARD METHODS for the examination of water and wastewater.

Analysis of chloride

Chloride was estimated as per the standards methods No.4500, page No. 4-72 of STANDARD METHODS for the examination of water and wastewater.

Analysis for degradation

The degradation and mineralization studies were performed by measuring COD of the samples during treatment. A full scan of bleaching effluent and treated effluent before and after treatment was also done in UV/VIS spectrophotometer, having a wavelength range from 190-900 nm. All the experiments reported were carried out in a 4 ml quartz couvette. Spectrophotometer is having both Tungsten and Deuterium lamp at operating temperature of 0-40^{o}C.

Biodegradability

Due to the high cost of photochemical processes, it must be taken care that target pollutants are definitively non-biodegradability since for easily biodegradable compounds, classical biological treatments are, at present, the cheapest and the most environmentally compatible.

A ratio of BOD_5/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD_5/COD is more than 0.4, wastewater has much biodegradability. Whereas, if BOD_5/COD ratio is less than 0.4, wastewater is difficult to be biodegraded.

To investigate the biodegradability of wastewater sample after photocatalytic treatment, COD and BOD of the samples after the treatment were measured.

4.5. Photocatalytic treatment

Photocatalytic treatment was done for effluents. The samples were treated and the various parameters like pH, catalyst dose, concentration of oxidant, were varied and optimized.

4.5.1. Preparation of Sample

Wastewater collected from paper industry was highly polluted and its characteristics are shown in Table 5.1. So to get the value within measurable range, bleaching effluent was diluted in the ratio of 1:1. Single distilled water was used for the all dilutions. RO reject water and treated effluent was subjected to photocatalytic treatment 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.

4.5.2. Procedure

Wastewater sample was treated in the presence of UV light and natural sunlight in photo reactor for optimized conditions. A known amount of sample (200 ml) was taken in glass bowl and covered with transparent thin foil; air was also supplied by the aerator during experiments. Sample was withdrawn at regular interval of time and filtered through the syringe filter. COD of samples was measured as per the standard methods. All tests were repeated for getting the reproducibility of results. The average values have been reported in the present studies.

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

CHAPTER 5

5. Results and Discussions

5.1. Paper mill wastewater characteristics

The raw wastewater sample BE was collected from homogenous tank from paper industry, Punjab. The BE was analyzed for various initial parameters such as BOD, COD etc. as shown in Table 5.1. Before photocatalytic treatment, BE was diluted in the ratio of 1:1 with single distilled water as it was highly concentrated. All experiments were done in triplicate and mean values were recorded. The conditions were optimized by varying the operational parameters to achieve the economy of the process.

S.No	Parameter	Bleaching effluent
1.	pH	4.12
2.	COD (mg l^{-1})	1920
3.	BOD (mg l^{-1})	593.035
4.	BOD/COD ratio	0.3088
5.	Conductivity (µs/cm)	1358
6.	Turbidity (NTU)	62.6
7.	TDS (mg l^{-1})	2160
8.	TSS (mg l^{-1})	260
9.	Chloride (mg l^{-1})	3540
10.	Sulphate (mg l^{-1})	12.16
11.	Color (Pt-Co units)	176 x 10

Table 5.1 Characteristics of bleaching effluent

All these parameter shows that the BE is highly polluted and exceeding the prescribed limit. The effluent presented high organic load in terms of BOD, COD, and color. The biological treatment is inefficient for the removal of color and complete degradation of chlorinated organic pollutants. High COD levels indicate toxic state of the wastewater along with the presence of biologically resistant organic substances. Low BOD_5/COD ratio of 0.3 indicated low biodegradability of the wastewater. Thus some sort of advanced treatment is required to overcome the drawbacks of conventional treatment or some sort of pretreatment is required to facilitate the biological treatment.

5.1.1. Absorption spectra for bleaching effluent

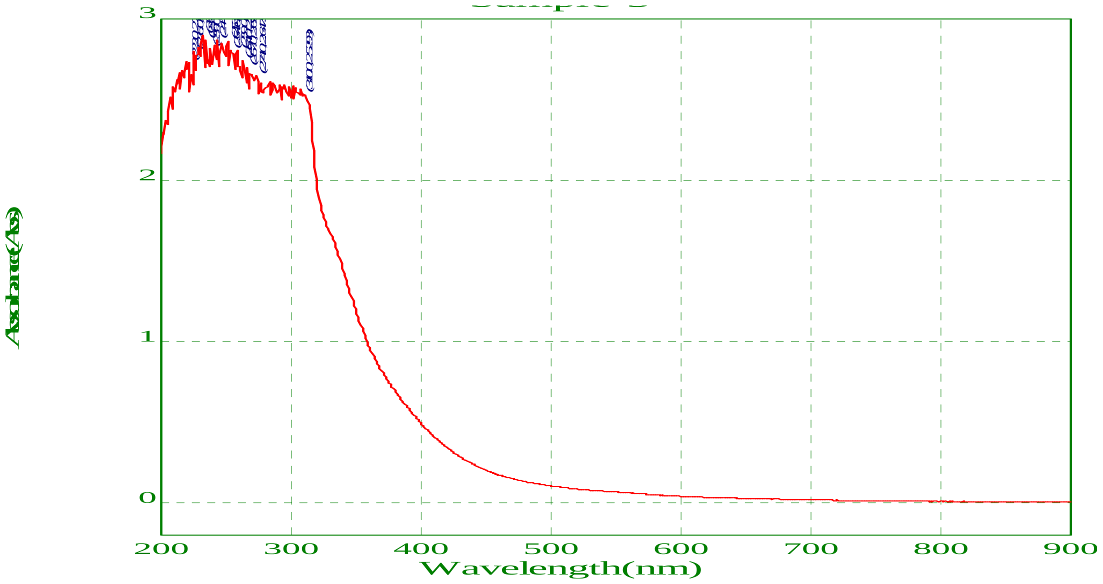

Figure 5.1 Absorption spectra of raw bleaching effluent

The absorption spectra (Figure 5.1) shows numerous peaks in the range of 200-350 nm which is in UV region thus confirming presence of various refractory compounds. Thus, there is a need of the treatment studies for the complete mineralization. COD is an important measure of water pollution and is necessary to be monitored during the photocatalytic degradation of bleaching effluent. Hence degradation of organic matter present in the effluents was monitored in terms of percent COD removal.

5.2. Preliminary study

The degradation of BE in dark (catalyst only) was negligible (5%) and in absence of catalyst (light only) was observed around 12%. This can be explained as photon as well as catalyst surface is required for adsorption for the reaction to take place. The use of oxidant (H_2O_2) also shows very minute degradation (2%). The reason is due to the generation of some OH radicals is not sufficient for reaction to take place **(Pokhrel D. and Viraraghavan T., 2004).** The oxidant along with UV light shows less degradation (17%) as catalyst surface is required for complete reaction to take place.

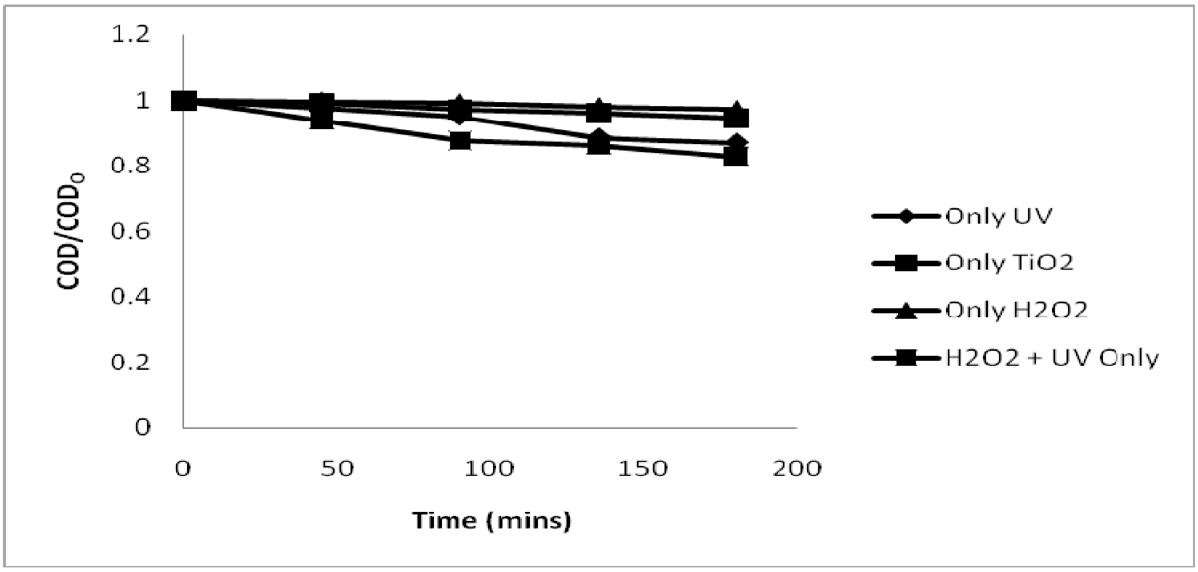

Figure 5.2 Preliminary study of bleaching effluent

5.3. Photocatalytic treatment

The preliminary studies suggest the need of effective treatment for the complete degradation and mineralization. Therefore, advanced oxidation process is suggested to BE to make it fit for disposal to natural water bodies or go for biological treatment. The BE 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.

5.3.1. Influence of initial pH

pH plays an important role in photocatalytic oxidation processes because pH affects the production of hydroxyl radical which is powerful oxidizing agent **(Balcioglu I.A. and Arslan I., 1998).** Thus the pH of BE was varied from 3.0 to 10.0 at 1.0gL^{-1} of catalyst dose during photocatalytic treatment and it was found that with increasing pH and decreasing pH there is decrease in degradation rate. At increased pH, there is a columbic repulsion between negatively charged surface of catalyst and the hydroxide anions which prevent the formation of $^{\cdot}$OH and decreases the photocatalytic degradation. At decreased pH, TiO_2 particles tend to agglomerate and surface area available for adsorption **(Kumar P. et al., 2011).** Maximum degradation of 79% was observed at pH 7.0 and the final pH after photo catalytic treatment was 7.8 which is suitable for biological treatment as well as discharge of wastewater into the water bodies (Figure 5.3).

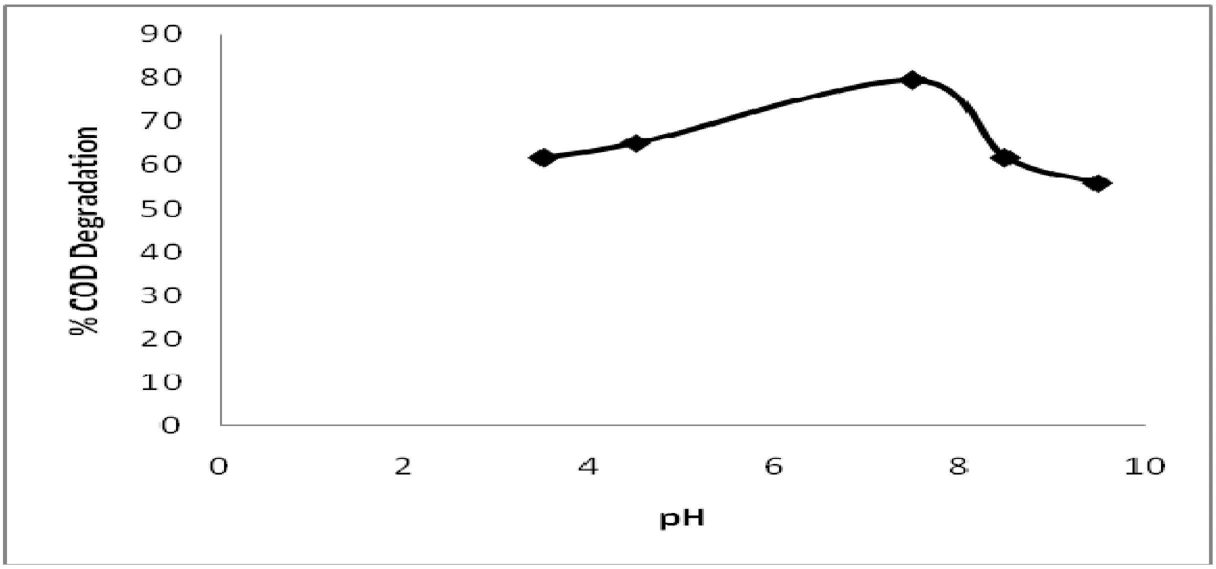

Figure 5.3 Effect of pH on % COD removal at 1 g L^{-1} of catalyst loading

5.3.2. Variation of catalyst (TiO_2) dose

The COD removal of BE was significantly improved by addition of catalyst but in order to economize the process at the industrial scale catalyst dose must be optimized. The efficiency in the rate of effluent degradation was determined by varying the concentration of photocatalyst (TiO_2) from 0.05 g L^{-1} to 4 g L^{-1} at constant pH 7.0 during the photocatalytic treatment for its optimization. The degradation efficiency was found to first increase up to catalyst dose of0.5gL^{-1} and then decreases. This is due the fact that a larger amount of photons that are absorbed by catalyst, thus accelerating the process **(Balcioglu A.I. and Cecen F. T., 1999).** The maximum degradation (79%) occurred at catalyst concentration 0.5 g L^{-1} (Figure 5.4). It is also observed that the efficiency of photo catalytic process increases with increase in catalyst concentration up to a certain limit and then becomes constant and starts to decrease after certain limit. The reason for 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 **(Toor A.P. et al., 2007).** Also, decrease in opacity and an enhancement of the UV light scattering by TiO_2 particles at higher concentration results in interruption in the passage of radiation through the wastewater sample.

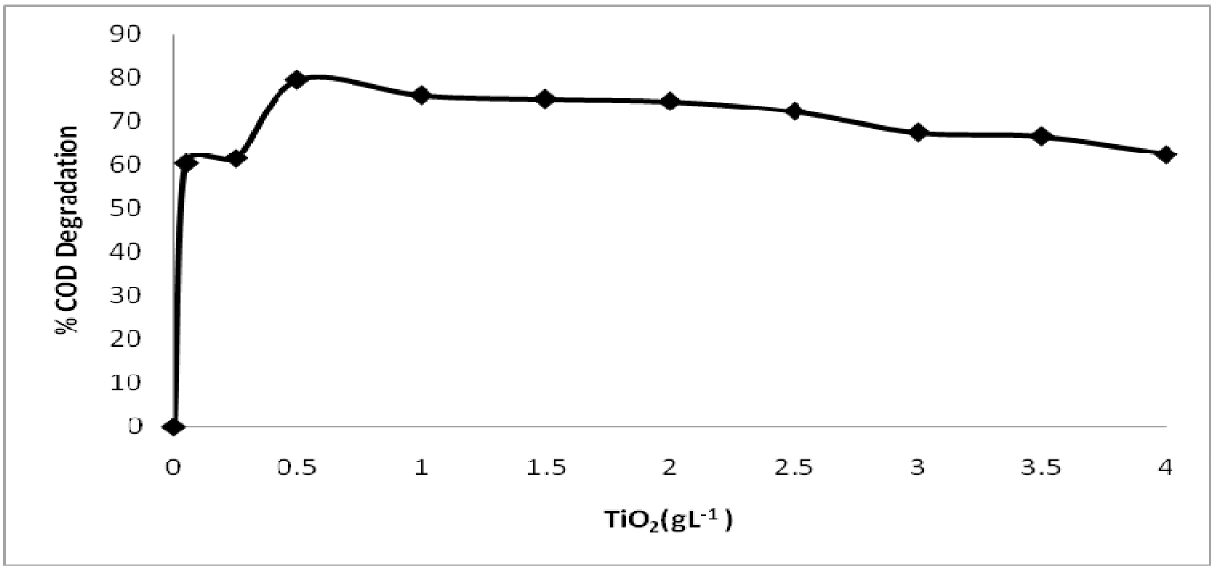

Figure 5.4 Effect of catalyst concentration on % COD removal at pH 7

5.3.3. Effect of oxidant dose

The addition of powerful oxidizing species such as H_2O_2 or $K_2S_2O_8$ to TiO_2 suspensions is a well known procedure to increase the concentration of $^{\cdot}OH$ radicals to promote the reaction of photocatalytic degradation **(Paillard H. et al., 1988).** H_2O_2 is considered to have two functions in the process, one is to accept photo-generated electron from the conduction band and thus promotes the charge separation (Eq 3) and secondly forms $OH^{\cdot}$ Radicals (Eq 4).

$H_2O_2 + e- \rightarrow OH^- + OH^{\cdot}$ **(3)**

$H_2O_2 + O_2 \rightarrow OH^{\cdot} + OH^{\cdot} + O_2$ **(4)**

During experimentation, the concentration of oxidant was varied from 0.5 ml L^{-1} to 2.5 ml L^{-1} at fixed TiO_2 dose (0.5 g L^{-1}) and at constant pH (7.0). The Results interpret that the degradation rate increases from the 79% to 86% (Figure 5.5).

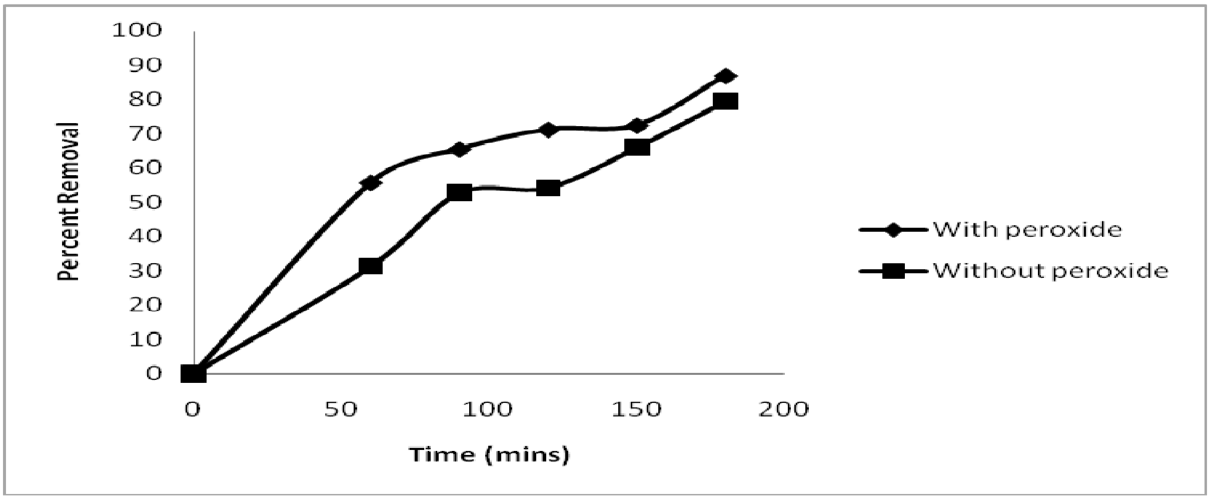

Figure 5.5 Comparison of COD removal rate with and without peroxide during photocatalytic treatment

The best result were obtained when oxidant addition was 2 ml L^{-1} and have been taken as the optimum amount required more maximum effective treatment of pollutant (Figure 5.6). 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 **(Nicole I. et al., 1991).** The increase by hydrogen peroxide is due to the production of hydroxyl radical by photo-dissociation of H_2O_2 which is acting as strong oxidant and as electron scavengers **(Toor A.P. et al., 2005).** At high concentration of H_2O_2 , it acts as scavengers.

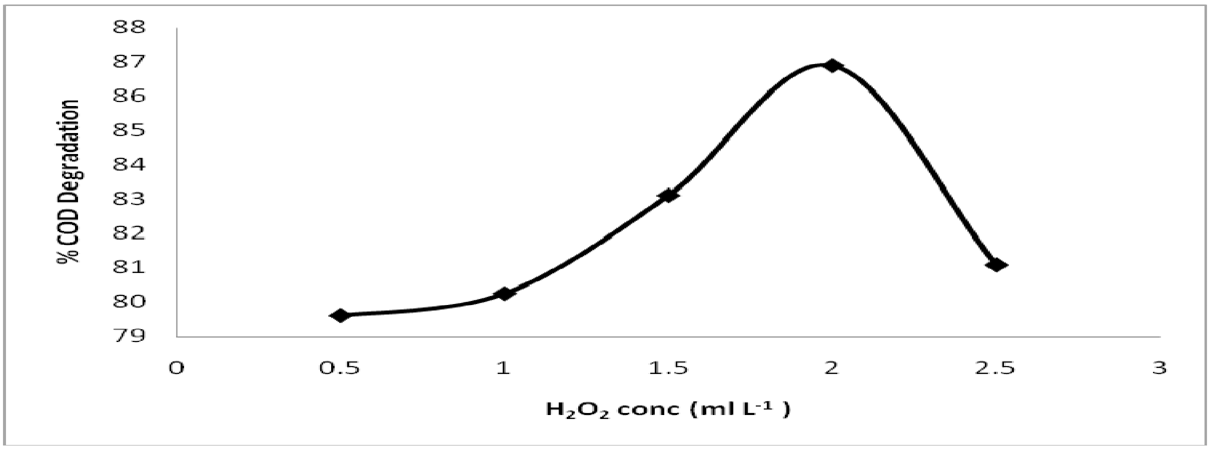

Figure 5.6 Effect of oxidant concentration on % COD removal at 0.5 g L^{-1} of catalyst loading

5.3.4. Effect of intensity

The amount of degradation depends on the radiation intensity. Various researchers have found that the reaction rate increases with the square root of intensity at high levels, but changes to a first-order relationship at lower levels of illumination. The degradation studies of BE was done below 30 Wm^{-2}, thus the dependence of rate constant on intensity was of first order. The experiments were conducted with all optimum conditions in the shallow slurry pond reactor under artificial light at three different intensities of 10, 18, 27 W/m^2 .The degradation rate constant increases with increase in intensity and best results are obtained at 35 W/m^2 (Figure 5.7). At higher intensity, the electron-hole formation is predominant and hence electron-hole recombination is negligible **(Bajpai P., 2000).** At lower intensity, electron-hole pair separation competes with recombination which decreases formation of free radicals causing lower degree of degradation.

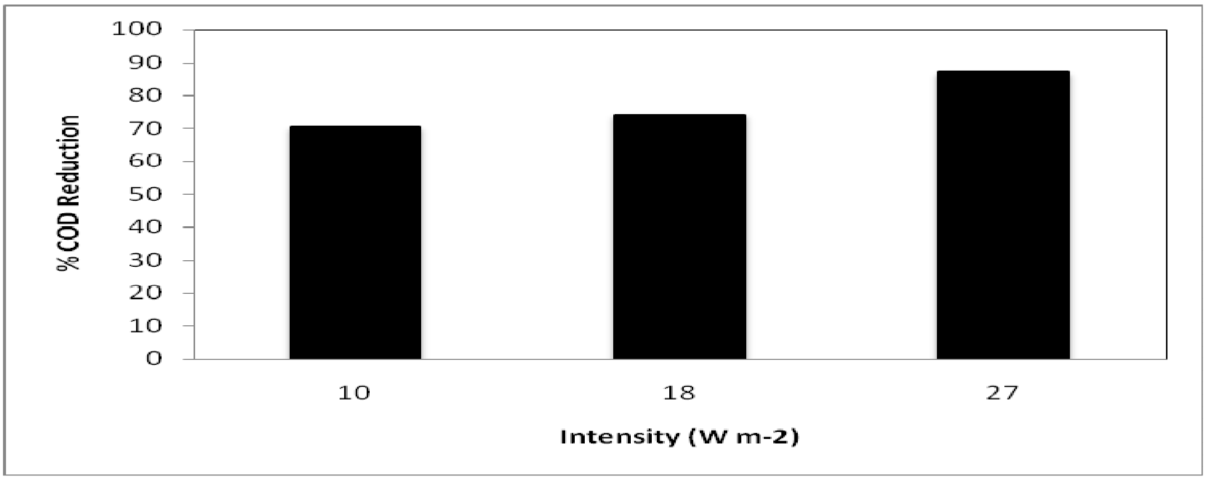

Figure 5.7 Effect of UV intensity on % COD removal

5.3.5. Solar studies

The experiments were conducted with all the optimum conditions (0.5 g L^{-1}, 2 ml L^{-1}, pH 7) in shallow pond type reactor under natural sunlight. India being a tropical country, there is a free availability of sunlight. To make the full use of sunlight and make treatment economical, sunlight is preferred for the wastewater treatment **(Amat A.M. et al., 2005).** Hence, all experiments were done in the months of March, April, May between 9.30 am to 5pm to harness maximum solar radiation. The degradation rate is a function of irradiation time on illumination of an aqueous suspension of wastewater sample in the presence of TiO_2 (Degussa P25, 0.5 gL^{-1})

under sunlight and UV light source, respectively **(Dubey S.K., 2009).** It was observed that the extent of degradation of the wastewater sample was little more in the presence of solar light (91%) as compared to UV light (86%) (Figure 5.8).

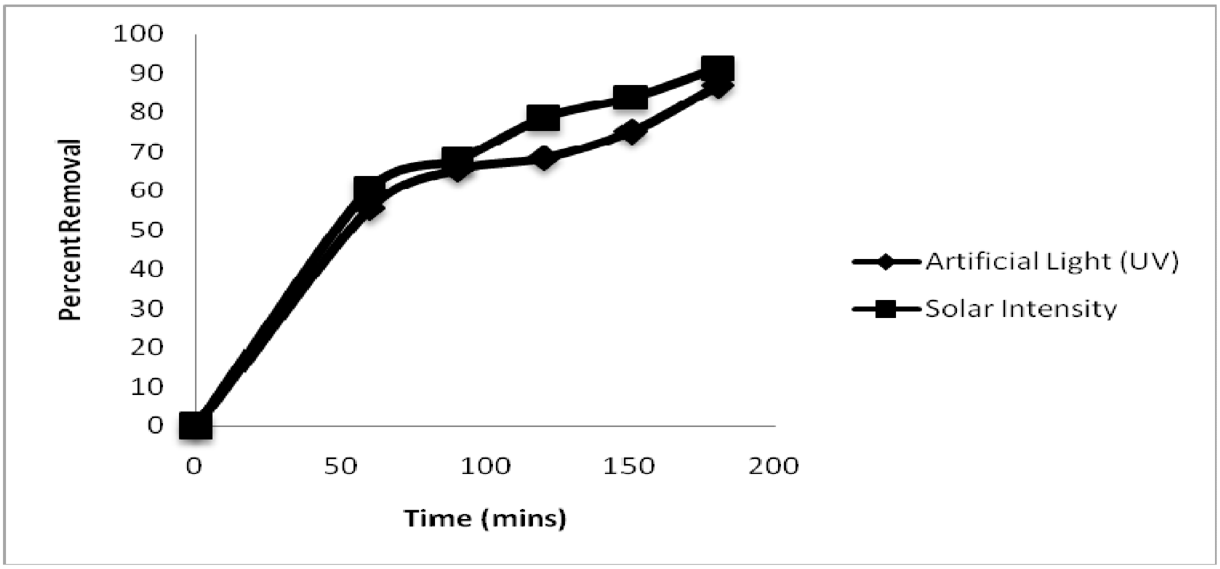

Figure 5.8 Comparison of COD removal rate with UV intensity and solar intensity during photocatalytic treatment

A significant removal of COD of BE was observed in the SOLAR/TiO_2/H_2O_2 as compared to other AOP treatment methods (Figure 5.9). Results confirmed the viability of scale-up of photocatalytic process with certain expert modifications for defining the economics of process. **(Wyness, P. et al.,1994).**

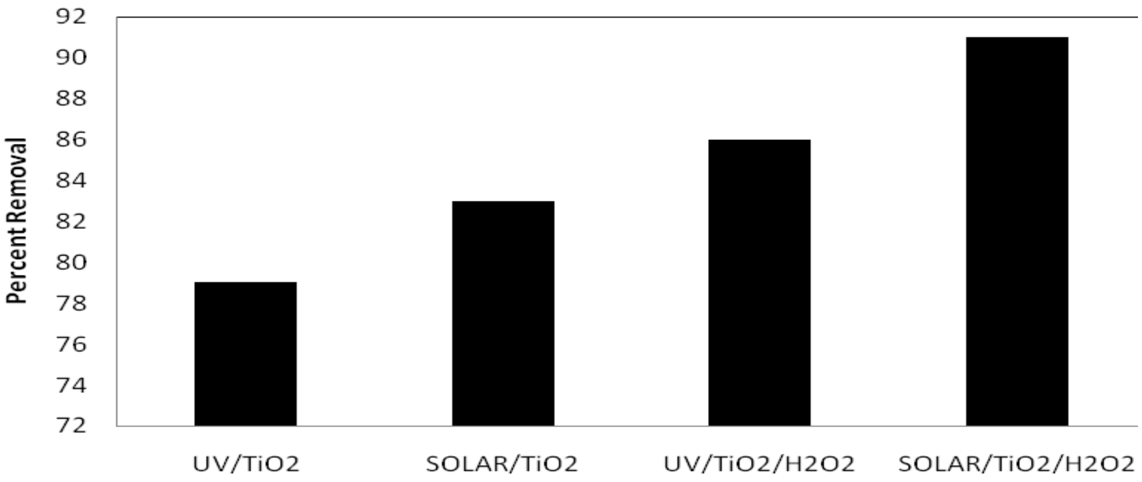

Figure 5.9 Comparison of COD removal rate during photocatalytic treatment

5.3.6. Kinetic analysis of TiO_2 photocatalysis

For more knowledge of degradation and decolourization of BE, all the oxidation processes are described in terms of first order kinetics. First order rate constant was calculated by the slope of –ln (C/C_0) *vs* t (min), where C and C_0 are the concentrations at time t and $t_{initial}$, respectively.

Experiments	Value of K in min^{-1}
UV/TiO_2	0.007
$UV/TiO_2/H_2O_2$	0.010
$SOLAR/TiO_2$	0.009
$SOLAR/TiO_2/H_2O_2$	0.013

Table 5.2: Value of k of different photocatalytic treatment

The values of k were compared for different experiments and table 5.2 depicted that UV/TiO_2 photocatalysis has lower value of k in comparison with $UV/TiO_2/H_2O_2$ photocatalysis. In case of $Solar/TiO_2/H_2O_2$, value of k is highest due to increases of degradation and decolourization capacity in the presence of both hydrogen peroxide and sunlight.

5.3.7. Bleaching effluent characteristics after photocatalytic treatment

After the photocatalytic treatment in UV/solar reactor under optimized conditions (TiO_2 dose of 0.5 g L^{-1}, pH of 7.0, and oxidant dose of 2 ml L^{-1}), characterization of the treated wastewater was done. The table 5.3 shows the parameter analyzed after the 3 hrs of photocatalytic treatment of BE which shows a major reduction in pollution load.

S.No	Parameter	Prevailing Range
1.	pH	8.3
2.	COD (mg l^{-1})	178
3.	BOD (mg l^{-1})	83.6
4.	BOD/COD ratio	0.588732
5.	TDS (mg l^{-1})	584
6.	Turbidity (NTU)	14
7.	Conductivity(µs/cm)	627
8.	Chloride (mg l^{-1})	1340
9.	Sulphate (mg l^{-1})	8.4
10.	Color (Pt-Co)	113

Table 5.3 Characteristics of bleaching effluent after treatment

The other parameters like COD, BOD and BOD_5/COD ratio as examined after treatment shows the 91% reduction in COD, 86% BOD. The increased BOD_5/COD ratio reduces load on biological treatment. 93% colour reduction is observed and a small reduction was observed in sulphate concentration. A considerable reduction was observed in TDS (72%) and chloride concentration (62%) for wastewater sample so this can be used as a preliminary treatment step before applying other conventional treatment technologies.

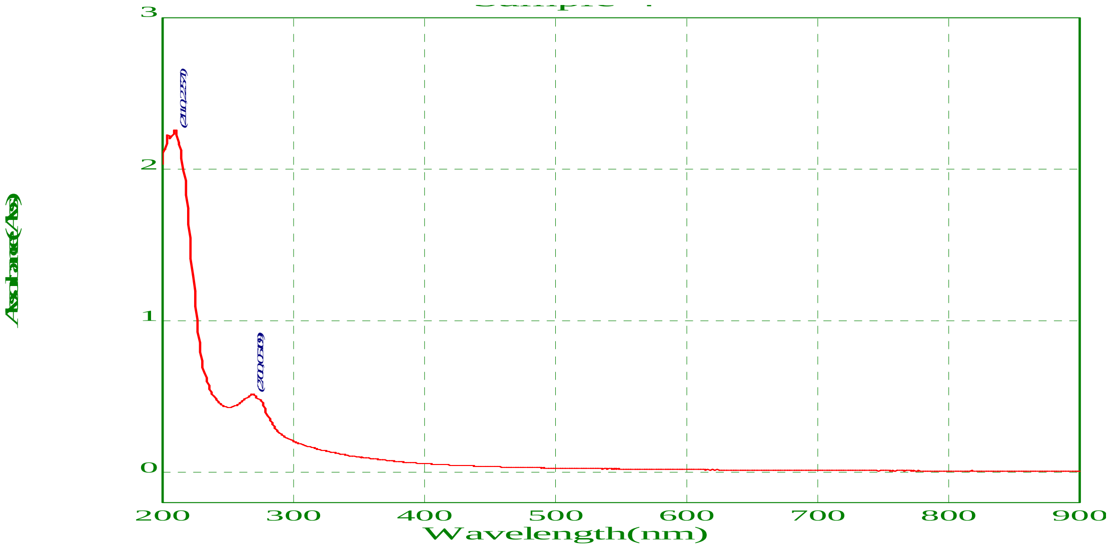

Figure 5.10 Absorption spectra of bleaching effluent after treatment

As the reaction proceeds, the peaks as observed in figure 5.1 disappear gradually as shown in figure 5.10 and the full scanning spectrum pattern changes. At the end of the 3 hrs of reaction time, there is no evident peak observed. It proves that organic chromophoric compounds in effluent is fully decomposed under Solar+TiO_2+H_2O_2 system.

5.3.8. Biodegradability

The biodegradability of the pollutants present in the effluents was estimated in terms of the BOD_5/COD ratio **(M. C. Yeber et al., 1999)**.The initial biodegradability index of the effluents was low i.e. 0.3 indicating that biorefractory organics are present **(Oller, I. et al., 2011).** For complete biodegradation, the effluent must present a biodegradation index of at least 0.40 **(Boman B. et al., 1989).** As can be seen in the Figure 5.11, moderate improvement in biodegradability index (BOD_5/COD) has been observed, the values being 0.50 and 0.58 with UV/TiO_2 and UV/TiO_2/H_2O_2 treatment systems, respectively. The results confirm that photocatalytic treatment can be opted for pre treatment in case refractory compounds are present in wastewater inhibiting their biological treatment.

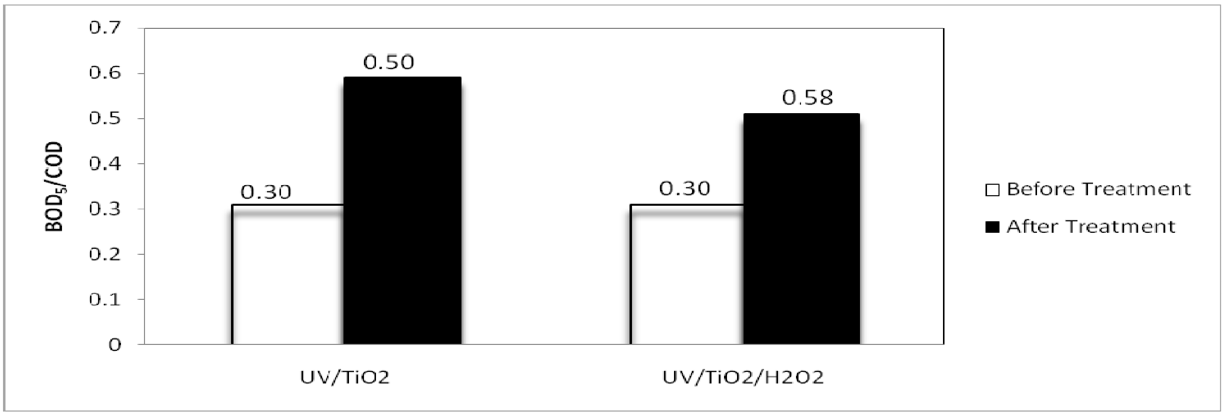

Figure 5.11 Comparison of biodegradability of UV/TiO_2 and UV/TiO_2/H_2O_2 treatment

5.4. Reuse of catalyst (TiO_2)

The process economics can be improved by reusing catalyst for photocatalytic process. In this view, the solar photocatalytic process was performed with three–four effective recycling of catalyst. The catalyst was recovered after each set (3 hrs) of optimized photocatalytic treatment by filtration through Whatmann filter paper No. 44. The catalyst recovered was then activated at 100°C (or open solar drying). The reduction in amount of catalyst was compensated by addition of fresh catalyst to the activated catalyst. Catalyst recycling depends up nature of pollutant, activation process, fouling of catalyst **(Verma A. et al., 2013).** The loss in activity of the catalyst with subsequent recycle can be attributed to the blocking of sites of TiO_2 due to surface fouling.

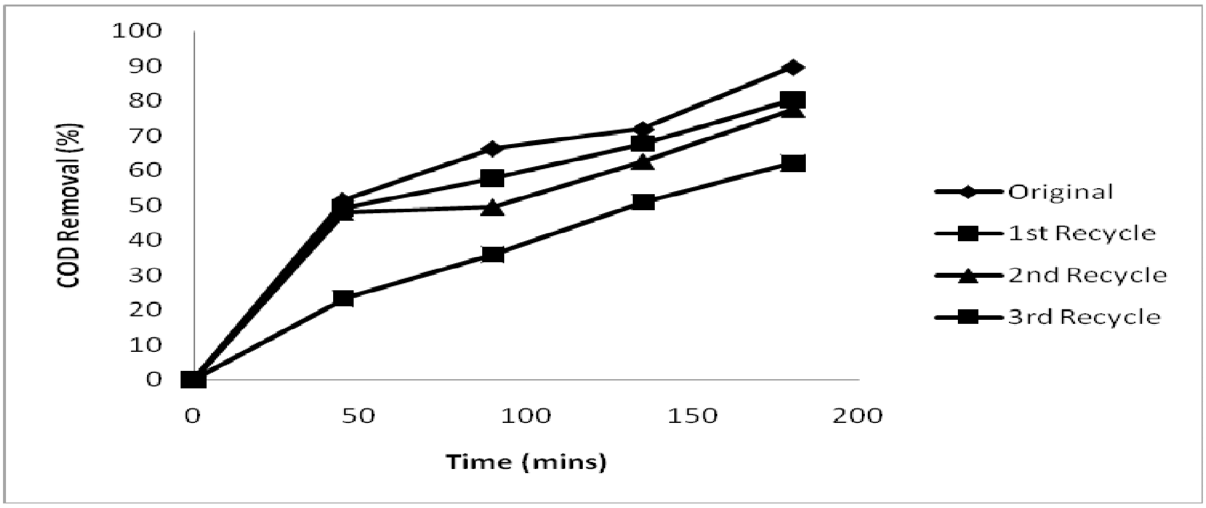

Figure 5.12 Recyclability of catalyst (TiO_2)

5.5. Viability of pre treatment of RO reject water

With the objective of the study, RWW was collected from the industry and subjected to photocatalytic treatment. The RWW was characterized for its parameter with TDS = 4750 mgL^{-1}. The efficiency of degradation was determined by varying the concentration of catalyst (TiO_2) from 0.25 g L^{-1} to 1 g L^{-1} at pH 7.0. The degradation was measured in terms of TDS reduction. The results were quite appreciable as there was 80% TDS reduction within 30 min of photocatalytic treatment with 0.5 g l^{-1} catalyst (Figure 5.13).

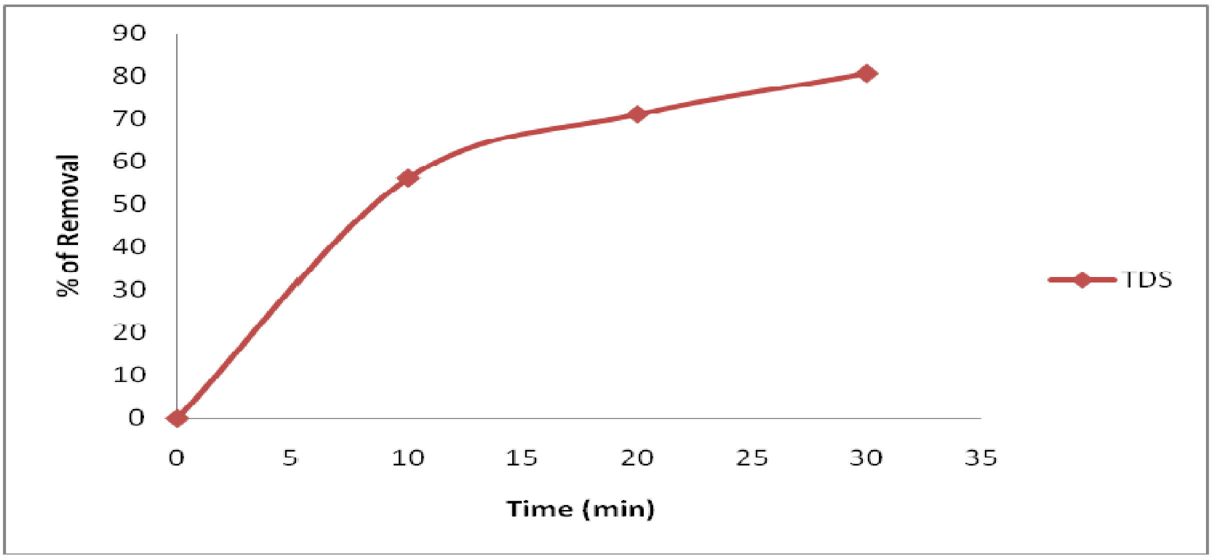

Figure 5.13 Removal of TDS during 30 min experiment with TiO_2

These results gave insight into the use of this treated reject water (TRW) for making commercial dilutions in industry or directly discard to plantation area/natural water source after treatment **(Afonso M.D. and Pinho M.N., 1991).**With this view, TRW was further used for preparing dilution of BE prior to advanced treatment. Here 20% dilution factor was used i.e. real wastewater was diluted with 20% AOP TRW and catalyst was recovered from RO reject photocatalytic treatment. The recovery of catalyst was done by filtration through Whatmann filter paper No. 44 and activated at 100°C (or open solar drying) and reused. The process efficiency decreases with increasing dilution factor. To keep the volume increase under control, the dilution factor should be appropriately chosen. Subsequently, the diluted real wastewater was subjected to UV photocatalysis and solar photocatalysis showing appreciable degradation. In future industrial application, fouling of membrane can be avoided by pre-treatment of reject water by photocatalysis. The retentate of reverse osmosis containing only inorganics can be passed through filtration (NF,UF,MF) and then can be reused for dilution or cooling. The TRW can be used for toiletry, bathing, plantation, washing work. The returns on account of chemical recovery can offset operating cost of effluent treatment recycling system.

5.6. Color removal of treated effluent

Removal of color from wastewater is often more important than the removal of soluble colorless organic substances, a major fraction of which contribute to the COD, BOD and toxicity besides disturbing the ecological system of the receiving water bodies **(Toor A.P. et al., 2007).** The traditional techniques used for removal of color are activated carbon (charcoal), filtration and coagulation, each having their own advantages and disadvantages. The use of charcoal is easy but has high waste disposal cost. Although filtration provides pure water as the final product, low molar mass pollutants are passed through the filter system. Coagulation using alums, ferric salts or limes is a low cost process, but all these methods have a major disadvantage of simply transferring the pollutants from one phase to another rather than destroying them.

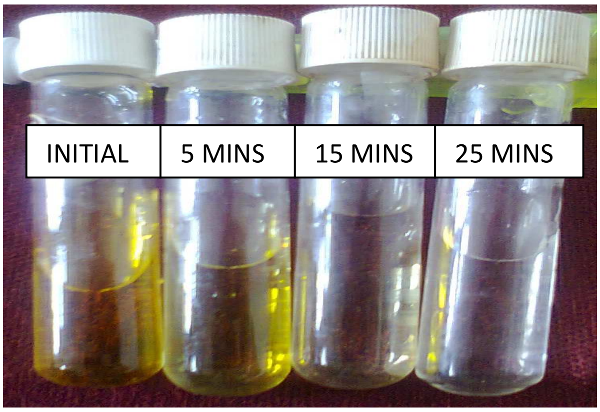

Figure 5.14 Color removal during photocatalytic treatment

Color is observed in the wastewater due to presence of lignin which is significantly removed after UV/solar photo catalytic treatment with optimized conditions i.e. 7.5 pH, catalyst concentration of 1 gL^{-1}. Figure 5.15 shows the effectiveness of solar photo catalysis for reduction of color of sample wastewater, the color reduction is 95% after 25 min of treatment and sample is completely discolored after completion of the reaction. The decolorized treated effluent can be reused for plantation.

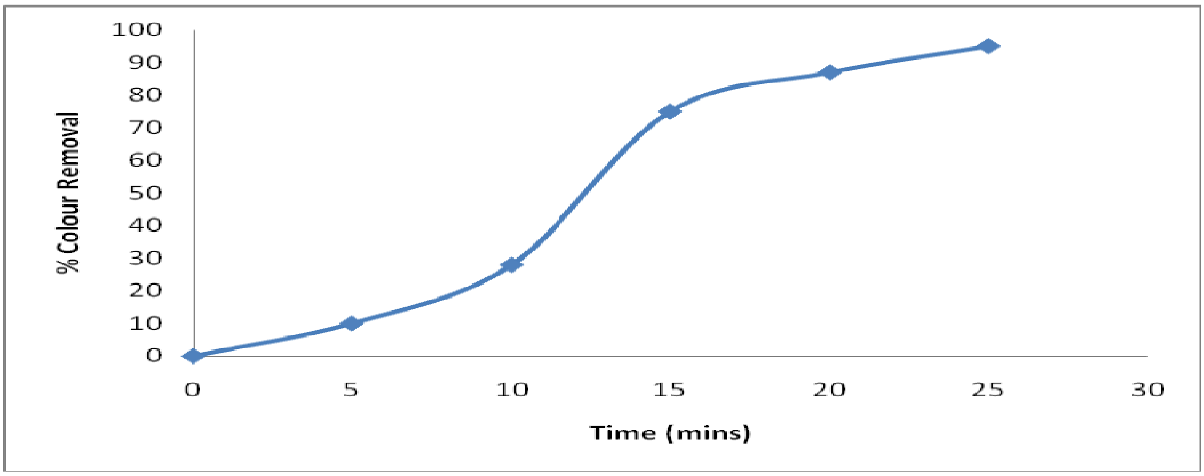

Figure 5.15 Removal of color from treated effluent during photocatalytic treatment

5.7. Fixed bed photocatalysis

In recent years, several different types of solar photocatalytic reactors coated with TiO_2 have been developed for waste water treatment. In this study, glass plate solar reactor was designed as a sloping flat plate reactor coated with catalyst: P25 Degussa TiO_2 **(Jayant S., 2012).** Moreover to the best of our knowledge, no studies have been done in literature for degradation of effluents using fixed bed. The experiments were performed using glass plate solar reactor with all the optimum conditions (BE:-TiO_2=0.5 g L^{-1}, pH 7.0, H_2O_2=2 ml L^{-1} and TE:- TiO_2=1 g L^{-1},pH 7.5). achieved in slurry type reactor. The results shows (figure 5.16) 70% and 86% degradation of BE and TE was observed after 8 and 3 hours of irradiation, respectively.

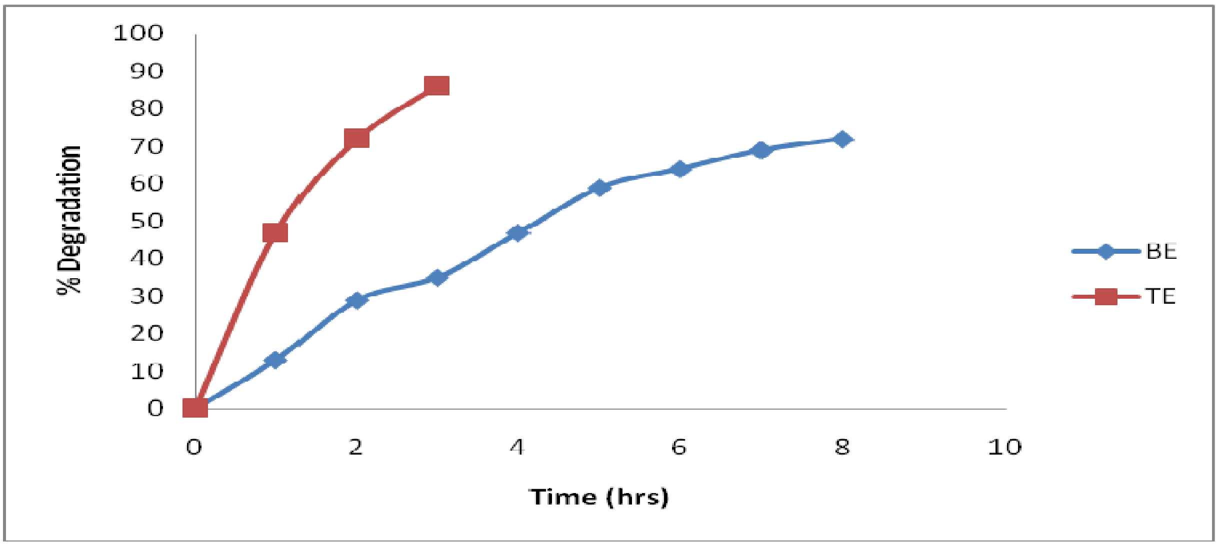

Figure 5.16 Degradation by glass plate solar reactor at the optimum conditions

CHAPTER 6

6. Conclusion

In the near future, advanced oxidation process may become most widely used technologies for organic pollutants as they are not treatable by conventional techniques due to their high chemical stability and low biodegradability. Heterogeneous catalysis using sunlight provides an alternative and effective method for mineralization. Combination of AOP_s as preliminary treatment method with inexpensive biological process seem very promising from an economical point of view.

From the results of our experiments it can be concluded that photocatalytic treatment using TiO_2 and UV light in a shallow pond type reactor can efficiently remove COD of bleaching effluent. The experiments demonstrate that choosing of optimum degradation parameters is required for higher degradation rates. $UV/TiO_2/H_2O_2$ treatment process is much more efficient than UV/TiO_2 treatment process due enhancement of the photoprocess performance. Experiments carried out in sunlight gave results better than those obtained in laboratory conditions. Photocatalysis should be applied as a pre-treatment technique, because increased value of BOD_5/COD ratio is obtained which increases the biodegradability of the effluent moderately and improve water quality. The quality of treated effluent is improved by removal of its color. The use of aqueous suspension is limited for practical application by filtration problems due to the small size of TiO_2 particles. Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of removing the catalyst.ith regard to the photocatalytic treatment of RO reject water, moderate results were obtained that were mainly focused on the reduction of TDS and pollutant load that accumulate and cause high environmental impact. The high cost of TiO_2-photocatalysis technology may limit their application. To overcome this hurdle, we try to implement the idea of using treated RO reject water for dilution with bleaching effluent. This combination can help in achieving almost total reuse of the chemical dosage such as catalyst (TiO_2). A solar version of this process might also reduce much of the high energy cost that has been associated with this treatment. A schematic diagram of general strategy of wastewater treatment is devised (Figure 6.1). Much accurate method is needed to develop for modeling the kinetics of RO reject water. Further experiments need be conducted to test more treatment conditions and to study the process at the pilot scale.

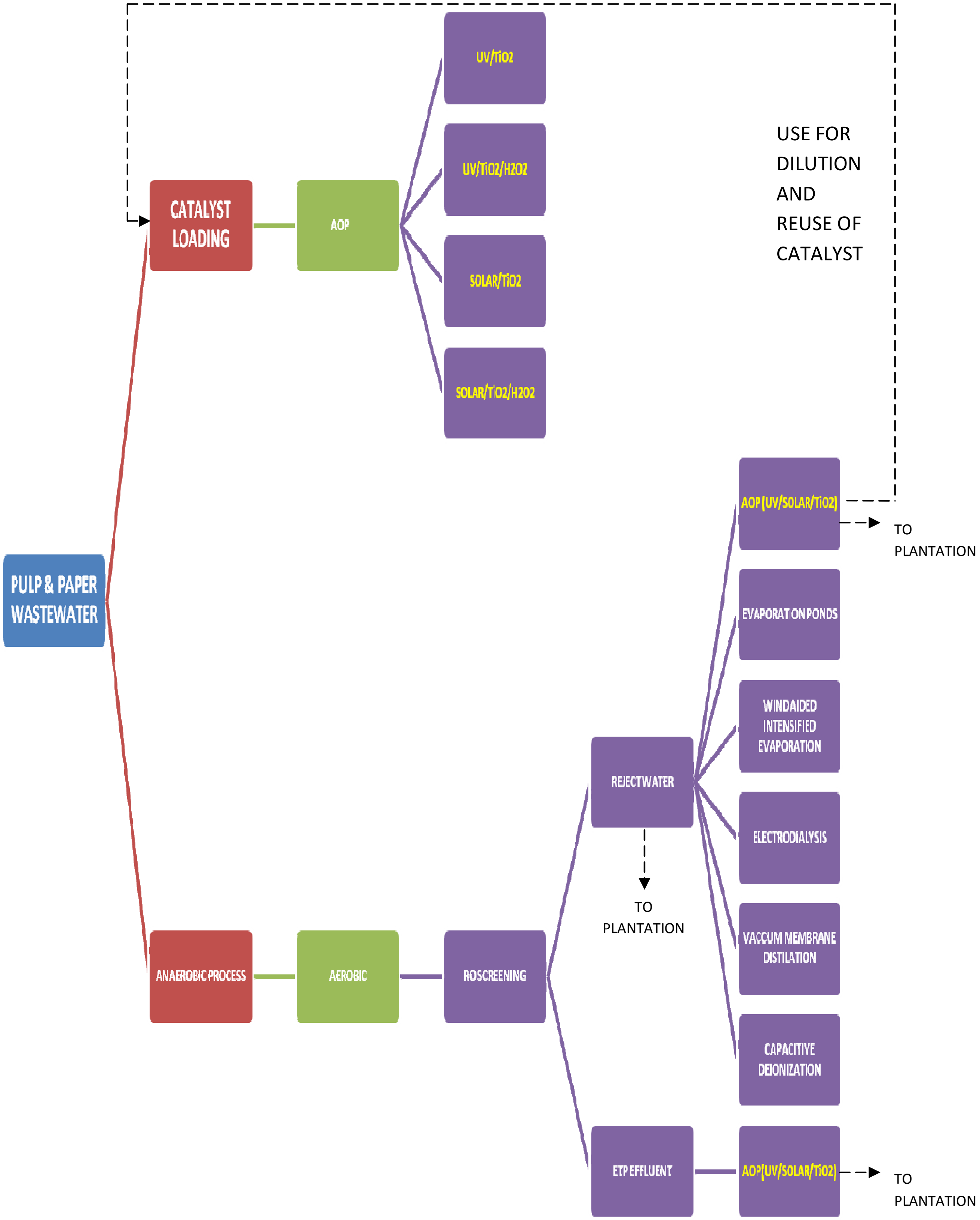

Figure 6.1 General devised strategy of wastewater treatment

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Publications

Conferences

- Anoop Verma, **Arpita Debnath** and Gurpreet Singh, "Degradation of Reactive Black 5 with dilution of treated RO Reject Water using Photocatalysis" A poster presented at RACES held at M.M. Modi College, Patiala, 31st Jan 2013.

- Anoop Verma and **Arpita Debnath**, "Treatment of Paper Mill Effluent by Photocatalytic Oxidation" A paper presented at NCRAREES 2013 held at Shoolini University, Solan, 8th & 9th June 2013.

- Anoop Verma and **Arpita Debnath**, "Optimization of degradation studies of paper mill effluents by TiO_2 photocatalysis" AOP 2013 to be held at Thapar University, Patiala, 21st-23rd November, 2013.

Journals

- Anoop Verma, **Arpita Debnath** and Gurpreet Singh, "Degradation of Reactive Black 5 along with dilution of RO Reject Water using Photocatalysis" Research Journal of Chemistry and Environment (communicated).

- Anoop Verma, **Arpita Debnath** and Gurpreet Singh, "Degradation and decolorisation studies of paper mill effluents by TiO_2 photocatalysis" Research Journal of Chemistry and Environment (communicated).

- Anoop Verma, **Arpita Debnath** and Gurpreet Singh, "Optimization of Fenton-biological treatment scheme for the treatment of textile effluent" Research Journal of Chemistry and Environment (communicated).

Awards

- Secured 2nd position in poster presented at RACES held at M.M. Modi College, Patiala, 31st Jan 2013.