Studies on coupled photocatalytic and biological process for degradation of pulp and paper mill effluent

A thesis submitted in partial fulfilment of the requirement for the award of the degree of

DOCTOR OF PHILOSOPHY

by

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Certificate

Certified that the thesis "Studies on Coupled Photocatalytic and Biological Process for Degradation of Pulp and Paper Mill Effluent" which is submitted by Mr. Amit Dhir, in fulfillment of the requirement for the award of the Degree of Doctor of Philosophy in the Department of Biotechnology & Environmental Sciences, Thapar University, Patiala, is a record of candidate's own independent and original research work carried out by himself under our supervision and guidance. The material embodied in this thesis has not been submitted in part or full to any other University or Institute for the award of any degree.

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Candidate's Declaration

I, hereby declare that the work presented in the thesis entitled "Studies on Coupled Photocatalytic and Biological Process for Degradation of Pulp and Paper Mill Effluent" in fulfillment of the requirement for the award of the Degree of Doctor of Philosophy, Department of Biotechnology & Environmental Sciences, Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of Dr. N. Tejo Prakash, Associate Professor, Department of Biotechnology & Environmental Sciences, Thapar University, Patiala, India and Dr. Dhiraj Sud, Professor, Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal, India. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree in India or Abroad.

Place: Patiala

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Executive Summary

The present study facilitated exploring avenues for examining cost effective solutions to treat pulp mill effluents containing chlorinated substituted organics. The research primarily focussed on the degradation of bleach as well as combined pulp and paper mill effluents by coupling of heterogeneous photocatalysis with conventional biological treatment. Photocatalytic degradation of the model compounds such as 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG) typically found in bleach mill effluent was examined using different photocatalysts (TiO_2/ZnO) under UV/solar light irradiation and the degradation efficiency was investigated in terms of changing concentration of the compound by measuring the absorbance. Photocatalytic degradation of all model compounds (2-MP, 4-CC and 4-CG) was observed to be significant as compared to photolysis. The extent of photocatalytic degradation increased with increase in catalyst dose upto an optimum loading and is also pH dependent. ZnO was observed to be better degrading catalyst than Degussa P25 TiO_2 for the degradation of the model compounds and effluents. Moreover, ZnO exhibit better photocatalytic activity in the presence of solar light as compared to UV light. Use of sodium hypochlorite (NaOCl) as an oxidant along with TiO_2 as photocatalyst enhanced degradation efficiency however, NaOCl showed no effect with ZnO induced degradation. The increase in the concentration of the substrate was observed to decrease the extent of degradation. The reaction rate for the degradation of 4-CC and 4-CG was found to be pseudo-first order with respect to their concentration within the experimental range. Photodegradation kinetics was described by the Langmuir-Hinshelwood model. The degradation of the model compounds was further confirmed by COD/HPLC techniques. Mixed photocatalyst (ZnO and TiO_2 in the ratio of 9:1) was used and

found to have higher degrading efficacy for degradation of 4-chloroguaiacol (4-CG). The photocatalytic efficiency of synthesized heterostructured ZnO/TiO_2 photocatalysts (Z_9T) was more than ZnO (Merck) and Degussa P25 TiO_2 for the degradation of 4-CG at pH 10.

The C and E_1 stages bleach mill effluents were also subjected to independent biological, photocatalytic and coupled treatment systems. It was evident from the present study, that the coupling of solar assisted AOP - biological treatment processes or *vice versa*, based on the type of the effluent, proved beneficial over the either of the treatment systems independently, in reducing COD/TOC load. Qualitative and quantitative analysis of model compounds in C stage bleach mill effluents was evaluated using GC/MS technique and chromatograms confirmed the degradation of model compounds in C stage bleach mill effluent. An attempt was also made to introduce photocatalytic treatment as a part of the existing biological treatment (anaerobic followed by two stage aerobic treatment) being adopted in industrial ETP so as to maximize the degradation efficiency of combined pulp and paper mill effluents with little modifications and minimum input cost. The *stage-1* (UASB treated) and *stage-2* (sequential UASB-ASP-I treated) effluents were subjected to sequential photocatalytic-biological (aerobic process) treatment.

It is concluded from the present study that photocatalytic treatment may be placed after the existing UASB-ASP-1 treatment to achieve integrated anaerobic-aerobic-photocatalytic-aerobic sequential processes for the enhanced degradation of recalcitrant contaminants present in the pulp and paper mill effluents. The fixed catalyst approach was also employed for *stage-2* effluents using ZnO under solar mode and the immobilized mode achieved lesser degradation as compared to slurry mode but the former is practically more applicable at industrial level.

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" With the Grace of All Mighty seed of thought flourished into sapling
In deed God and Guide work hand in hand "

Pursuing Ph.D. degree is a both painful and enjoyable experience. It's just like climbing a high peak, step by step, accompanied with bitterness, hardships, frustration and encouragement. When I found myself at the top enjoying the beautiful scenery, I realized that it was in fact, team work that got me there. I would like to take this opportunity to thank all people who have helped and encouraged me through out this study. It is a pleasant aspect that I have now the opportunity to express my gratitude to all of them.

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Dedicated to my Parents

h	Hours
d	Days
rpm	Revolution per minute
g	Gram
L	Litre
V	Volume of the solution
Ms/cm	Microsiemens per cm
mL	Millilitre
µg/L	Microgram per litre
mg/L	Milligram per litre
g/L	Gram per litre
M	Molar
mM	Milli Molar
N	Normality (normal)
%	Percentage
min	Minute
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
HPLC	High performance liquid chromatography
GC-MS	Gas Chromatography – Mass Spectroscopy
e.g.	For example
w.r.t.	with respect to
H_2SO_4	Sulfuric acid
NaOCl	Sodium Hypochlorite
HCl	Hydrochloric acid
LB	Luria Broth
nm	Nanometer
OD	Optical density
ETP	Effluent Treatment Plant
COD	Chemical oxygen demand
BOD	Biochemical oxygen demand

TOC	Total organic carbon
AOX	Adsorbable organic halides
TS	Total solids
TSS	Total suspended solids
TDS	Total dissolved solids
AOP's	Advanced oxidation processes
UASB	Upflow anaerobic sludge blanket digestor
ASP	Activated sludge process
2-MP	2-methoxy phenol
4-CC	4-chlorocatechol
4-CG	4-chloroguaiacol
BME	Bleach mill effluents
Raw	Primary clarified effluent sample from pulp and paper mill ETP
Stage-1	Effluent sample after anaerobic treatment from functional ETP
Stage-2	Effluent sample after sequential anaerobic-aerobic treatment from ETP
Bio	Biological treatment
Photo	Photocatalytic treatment
Photo-C	Photocatalytic treatment with TiO_2
Photo-C+O	Photocatalytic treatment with TiO_2/NaOCl
Solar/ZnO	Photocatalytic treatment with ZnO

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1.0 INTRODUCTION

Undoubtedly, water is the most precious natural resource that exists on our planet and comprises over 70% (≅ 1.4×10^9 Km^3) of the earth's surface. Only 0.8-1.0% (i.e.~1.3×10^7 Km^3) of the total water resources, corresponds to the drinking water [World Resources Institute 1994-95, N.Y.O., 1994]. Life on Earth would be non-existent without this seemingly invaluable component. World water consumption per year is about 9 x 10^3 km^3 and at present, the quantity of available potential drinking water per year is between 10 to 30 x 10^3 km^3. These figures clearly illustrate how even a small shortage of water could become a threat to mankind. Although human beings recognize this fact, but still disregard it by polluting rivers, lakes, and oceans. The rapid urbanization and industrialization is slowly but surely harming our environment to the point where organisms are dying at a very alarming rate. The situation even gets worsened due to lack of adequate wastewater treatment systems.

In the developing countries like India, surface water quality is deteriorating due to release of large amount of organic compounds being discharged in industrial effluents. The major sources of water pollution are municipal, industrial, and agricultural sectors. The characteristics of industrial wastewaters can differ considerably both within and among industries. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and the amount of suspended solids, but also on their content of specific inorganic and organic substances. Organic pollutants such as alkanes, haloalkanes, haloaromatics, herbicides, pesticides and dyes are commonly present in industrial effluents [Pandiyan et al., 2002]. These compounds are quite toxic and degrade slowly in the environment which leads to

number of adverse effects and disorders in human life. Therefore it becomes imperative to facilitate complete degradation of these organic compounds.

In order to combat water pollution, the efficient treatment of wastewater is practically essential. Water treatment has two important areas which require immediate attention namely contaminated drinking, ground, and surface waters, and wastewaters containing toxic or non-biodegradable compounds. The basic methods of treating industrial wastewater fall into three stages: primary treatment for the removal of suspended solids which includes grit removal, screening, grinding, and sedimentation; secondary treatment, which entails oxidation of dissolved organic matter by using biologically active sludge. Secondary treatment of wastewater is concerned with the removal of biodegradable organic, suspended solids, and pathogens. Tertiary treatment includes advanced biological methods and chemical as well as physical methods such as granular filtration, activated carbon absorption for the removal of biorecalcitrant dissolved solids [Horan, 1990]. Some of the treatment technologies may be selective but slow to moderate in destruction rate, or rapid but not selective, thus require appreciable reaction or energy costs. Other treatment processes can be limited by economic reasons, effluent characteristics, or tendency to form harmful by-products. The incapability of conventional wastewater treatment methods in effective removal of many biorecalcitrant pollutants and stringent pollution legislation necessitates the development of new efficient treatment systems.

1.1 PULP AND PAPER INDUSTRY

The pulp and paper industry is one of oldest of the core industrial sectors. The socio-economic importance of paper has its own value to the country's development as it is directly related to the industrial and economic growth of the country. Although paper has many uses, its most important contribution to modern civilization is its use

as a medium to record information. A profile of the history of pulp and paper manufacturing showed that Egyptians were the first to produce writing material by pasting together thin layers of the stem of papyrus plant**;** from which paper gets its name. However, it was the Chinese who developed the first authentic papermaking process and utilized their method of suspending bamboo or mulberry fibers as early as 100 AD. Later Europe and the Middle East used cotton and linen rags to make their paper, and by the 15th century France, Germany, Italy, and Spain had paper mills. First paper mill located near Philadephia in North America came up in 1690. America saw the first Fourdrinier machine in 1827. In the year 1854, the first manufacture of wood pulp was done using the soda process. In 1884, the most widely used kraft pulping process was developed by Carl Dahl [Smook, 1984]. Refinement and modification to this technology is a continuous process. The development of techniques such as continuous cooking, continuous multistep bleaching, and the use of chemicals like hydrogen peroxide and chlorine dioxide facilitated closed pulping and reduction of dioxin in bleach mill effluents [Ferguson, 1991].

The Indian Paper Industry accounts for about 1.6% of the world production of paper and paperboard. The estimated turnover of the industry is Rs 25,000 crore approximately and its contribution to the exchequer is around Rs. 2918 crore. The industry provides employment to more than 0.12 million people directly and 0.34 million people indirectly. The mills use a variety of raw material viz. wood, bamboo, recycled fibre, bagasse, wheat straw, sarkanda, etc.; approximately 35% are based on chemical pulp, 44% on recycled fibre and 21% on agro-residues. The geographical spread of the industry as well as market is mainly responsible for regional balance of production and consumption. With added capacity of approximately 0.8 million tons during 2007-08 the operating capacity of the industry currently stands at 9.3 million tons. Over all paper consumption (including newsprint) has now touched 8.86 million

tons and per capita consumption is pegged at 8.3 kg. Demand of paper has been hovering around 8% for some time during the period 2002-07 while newsprint registered a growth of 13%, writing and printing, containerboard, cartonboard and others registered growth of 5%, 11%, 9% and 1% respectively. So far, the growth in paper industry has yielded the growth in GDP on an average 6-7 per cent over the last few years. Paper consumption is poised for a big leap forward in synchrony with the economic growth and is estimated to touch 13.95 million tons by 2015-16. The futuristic view is that growth in paper consumption would be in multiples of GDP and hence an increase in consumption by one kg per capita would lead to an increase in demand of 1 million tons [http://www.ipma.co.in].

Paper manufacturing has been considered to be a major consumer of natural resources (wood, water) and energy (electricity) and also a significant contributor of pollutants to the environmental matrix. The pulp and paper industry is the third largest water consuming industry in the world. The average water consumption for 'wood based' large pulp and paper industries primarily producing paper or paper board products in developed countries vary from 30 to 70 m^3/tonne of product. Whereas, average water consumption in 'waste paper' based pulp and paper mills in developed countries varies from 8 to 10 m^3/tonne of product. India is the fastest growing market for paper globally. In India, around 905.8 million m^3 of water is consumed and around 695.7 million m^3 of wastewater is discharged annually by this sector. Even with the use of most modern and efficient operational techniques, about 100-150 m^3 of water is consumed to produce a ton of paper [NPC, 2001] which is far above the global best water consumption of 28.66 m^3/tonne (for large scale wood based pulp and paper mill) and this large gap is primarily attributed to the use of obsolete technology /equipments and poor water management practices. The huge amount of water requirement and consumption by the Indian pulp and paper industries has led to,

generation of large quantity of wastewater. The wastewater pollution due to pulp and paper industries is multidimensional, causing serious problems not only to the landmass fertility but also to the natural flora, fauna as well as aquatic bodies. Besides this, water at the threshold of becoming a scarce commodity due to lowering of the groundwater table, led to immense increase in cost for consumption of water.

The pulp produced by chemical pulping process is subjected to bleaching in order to enhance its brightness by the removal of residual lignin. In developing countries, the use of chlorine and chlorinated compounds like calcium or sodium hypochlorite followed by caustic extraction is common process for bleaching of pulp in all paper mills and this spent wash water may be reused or discharged as an effluent. Among the pulp and paper mill discharges, the bleach mill effluents are considered to be most polluting since organochlorines such as chloroderivatives of phenols, guaiacols, catechol and aliphatic compounds [Sharma et al., 1996a; Kansal, 2006] present in them are toxic, bio-accumulative and persistent in nature. It has been reported that production of one ton of paper contributes approximately 100 kg of colour imparting substances and 2-4 kg of organochlorines to the bleach plant effluents [Nagarathnamma et al., 1999]. The compounds responsible for the toxicity of chlorination (C) and alkaline extraction (E) stage effluents are chlorophenolics and their derivatives together with resins and fatty acids. The chlorophenolics and their derivatives are formed during the C-stage of pulp bleaching and are solubilized in the E-stage. The nature and amount of chlorophenolics formed will depend upon the nature of the lignin and the bleaching conditions. Out of 300 different compounds identified in bleached mill effluents, approximately 200 are chlorinated organic compounds. Such a huge quantity of wastewater with a large proportion of chloroorganics are harmful for humans and aquatic life due to their potential

carcinogenicity, mutagenicity and toxicity [Ali and Sreekrishnan 2001; karrasch et al. 2006].

Several forms of legislation have been passed in India in the recent decades to control water pollution. The Water (Prevention and control of Pollution) Act was enacted in the year 1974 and Water Cess rules in 1977. This has helped to control surface water pollution from industrial and municipal sources throughout the country. The standards had been formulated for the discharge of wastewater from different category of industries. The Indian standards for discharge of effluents from pulp and paper mill have been given in Table 1.1.

Table 1.1: Discharge norms for large scale agro residue based Pulp & Paper Mills (Writing and Printing Paper)

Parameter		Standard
pH	-	7.0 - 8.5
Suspended Solids	-	Less than 50 mg/L
BOD_5	-	Less than 30 mg/L
COD	-	Less than 350 mg/L
AOX	-	1 Kg/ton of paper
Water Consumption	-	150 m^3/ton of paper

Source: CPCB, New Delhi

1.2. TREATMENT TECHNOLOGIES

The treatment of pulp and paper industry is of great challenge due to the presence of large variety of organic compounds; some of them are biorecalcitrant in nature. Biological treatment is one of the most promising and viable technology in the treatment of industrial effluents. Earlier, aerobic lagoons were widely used in the treatment of pulp and paper mill effluents and later activated sludge process (ASP)

was introduced. The treatment process in modern pulp and paper mills constitute anaerobic-aerobic sequential treatment with a limitation of high quantity of adsorbable organic halides (AOX) which retard the recycling of wastewater. Various treatment technologies available for the degradation of pulp and paper mill effluents may be summarized as follows.

1.2.1 Biological Treatment

Biodegradation is defined as the biologically catalyzed reduction in complexity of chemical compounds [Alexander, 1994]. The general objectives of the biological treatment of wastewater are to coagulate, remove the non-settleable colloidal solids and to stabilize the contained organic matter [Metcalf and Eddy, 2003]. In industrial wastewater, the objective is to remove and reduce the concentration of organic and inorganic compounds. Biological treatment is the most common, economically and environmentally attractive technique of wastewater treatment in comparison with other physical and chemical techniques [Gogate and Pandit, 2004a]. Biological treatment is classified as aerobic and anaerobic treatment. The most rapid and complete degradation of the majority of pollutants is brought about under aerobic conditions [Riser-Roberts, 1998]. Aerobic processes could be carried out by suspended (activated sludge), attached (biofilm reactor, trickling filter, and rotating disk contactor) or combined (moving bed biofilm reactor) depending on the operating conditions and wastewater characteristics. The treatment efficiency is higher for attached growth than suspended growth processes and moreover, the sludge production is low. Among the various aerobic biological treatments, activated sludge process (ASP) is widely used especially in pulp and paper industries [Stephenson and Blackburn, 1998], ASP consists of aerated reactor where microorganisms grow by assimilating the pollutants in the wastewater and the solids are settled in a separate clarifier which works on the principle of sedimentation. The complex microbial

community used in the process is known as activated sludge and is mainly composed of aerobic heterotrophic bacteria. Wastewater can also be treated by anaerobic processes such as up-flow anaerobic sludge blanket (UASB), anaerobic fluidized bed reactor (AFBR), expanded granular sludge bed (EGSB), and anaerobic baffled reactor (ABR). In natural waters and soils, the mineralization or complete biodegradation of an organic molecule is almost always a consequence of microbial activity [Alexander, 1994]. A huge number of bacteria and fungi generally possess the capability to degrade organic pollutants. To achieve a successful biotreatment, the basic information include the nature and concentration of the xenobiotic compounds; presence and activity of the degrading microorganisms; and appropriate conditions of cultivation for the growth of the target microorganisms.

1.2.2 Advanced Treatment Processes

Biological oxidation is limited when the feeding water contains substances either recalcitrant to biodegradation, or inhibitory or toxic to the microbial systems. With increased environmental awareness and stringent international standards, research on developing newer and efficient clean technologies for the degradation of such pollutants has drawn more attention. Apart from the biological processes, various other advanced treatment processes include supercritical water oxidation (SWO), electrochemical oxidation, wet oxidation, adsorption (using activated carbon) and chemical oxidation. One of the most promising treatments to achieve near complete degradation of hazardous organic compounds is the use of Advanced Oxidation Processes (AOP's) involving the oxidation of these bio-recalcitrant organic compounds. AOPs were defined by Glaze et al. (1987) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification by attacking the majority of organic matter. These chemical processes led

to complete mineralization of organic matter and no toxic compound is produced during the reaction. The kinetics of these reactions are of first order for (OH•) radical concentration, and to the species to be oxidized. Rate constant in general are in order of 10^8-10^{10} s^{-1}, where the hydroxyl radical concentration between 10^{-12}- 10^{-10} M. The AOP's has been included in the list of best available technology (BAT) by U.S. Environmental Protection Agency (EPA) in the recent past [Al-Ekabi, 2000]. These AOP are useful complements to well established techniques like flocculation, precipitation, adsorption on granular activated carbon, air stripping or reverse osmosis, combustion, and aerobic biological oxidation. Table 1.2 shows the oxidation potential for oxidizing agent used in water treatments, it can be seen that the hydroxyl radical is among the most potential agents. Most of the organic compounds can be oxidized by OH•, however, some organics are not influenced by hydroxyl radicals which include acetic acid, oxalic acid, chlorides derivatives as chloroforms and tetrachloromethane. AOP's include homogeneous and heterogeneous photocatalytic processes, latter being more efficient in the degradation of these organic compounds.

1.3 HOMOGENEOUS ADVANCED OXIDATION PROCESSES

The applications of homogeneous AOPs (single phase system) to treat contaminated water involve the use of an oxidant to generate radicals in the presence of ultraviolet light, which attack the organic pollutants to initiate oxidation. The efficiency of the system depends on the production of strong oxidant species such as hydroxyl radicals, which are able to oxidize almost all organic pollutants. The major processes used for the homogeneous degradation are: Hydrogen peroxide (UV/H_2O_2), Ozone (UV/O_3), Hydrogen peroxide and Ozone ($UV/ H_2O_2/O_3$) and Photo-Fenton system (Fe^{3+}/ H_2O_2). UV light can be used in several ways but direct photolysis can occur only when the contaminant to be destroyed absorbs incident light efficiently.

However, similar activity is not exhibited in the case of UV/ ozone and UV/ hydrogen peroxide.

Table 1.2: Oxidation potential for oxidizing agents in acidic medium

Oxidant	Standard Reduction Potential (V vs. NHE)
Fluorine (F_2)	3.03
Hydroxyl radical ($HO^{\cdot}$)	2.80
Atomic oxygen ($O^{\cdot}$)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Perhydroxyl radical ($^{\cdot}O$-OH)	1.70
Potassium permanganate ($KMnO_4$)	1.67
Hypobromous acid (HBrO)	1.59
Chlorine dioxide (ClO_2)	1.50
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09
Iodine (I_2)	0.54

Source: Kansal, 2006

1.4 HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalysis involves the degradation of organic pollutants in slurry or immobilized mode using various semiconductors (TiO_2, ZnO, CdS and ZnS) as photocatalyst, which may be photoexcited with UV light at λ below 390 nm, to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidizing sites). These radicals are highly reactive and unselective oxidants which convert organic matter into simpler end products such as carbon dioxide and water thus, confirming total degradation [Serpone, 1997]. The process is heterogeneous because there are two active phases, solid and liquid. The major light based advanced oxidation processes

are shown in Figure 1.1. The important features of this process which makes it particularly attractive method for the treatment of contaminated effluents are:

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

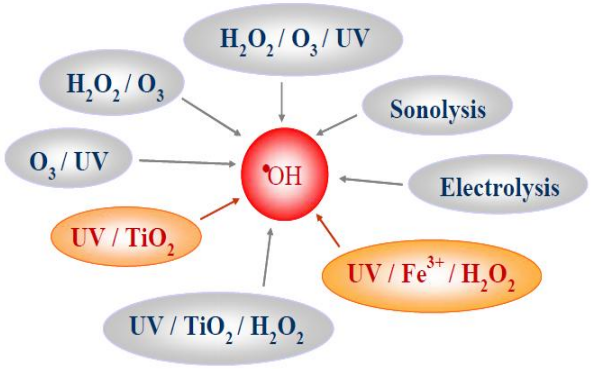


Fig. 1.1 Advanced oxidation processes

1.4.1 Mechanism of Photocatalysis

A semiconductor (SC) is characterized by an electronic band structure in which the highest occupied energy band, called valence band (vb), and the lowest empty band, called conduction band (cb), are separated by a band gap, i.e. a region of forbidden energies in a perfect crystal. When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the vb is promoted to the cb with simultaneous generation of a hole (h^+) in the vb. The e_{cb}^- and the h_{vb}^+ can recombine on the surface or in the bulk of the particle in a few nanoseconds (and the energy dissipated as heat) or can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. The holes are extremely oxidants and should thus be able to

oxidize almost all chemicals, as well as water, resulting in the formation of hydroxyl radicals [Munter et al., 2001]. Figure 1.2 **s**hows pictorial representation of the mechanism of TiO_2 photocatalysis.

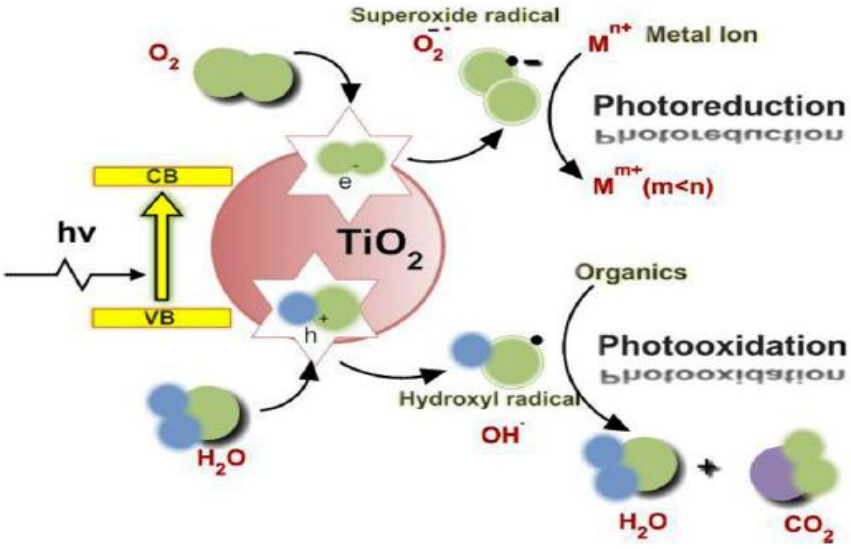


Figure 1.2: Mechanism of photocatalytic degradation under UV irradiation (Source: Vinu and Madras, 2010)

1.4.2 Photocatalyst

A variety of photocatalysts have been employed for decomposition of organic pollutants. Among the listed semiconductors, Titanium dioxide (TiO_2) which is otherwise used as white paint pigment, as sun blocking material, as cosmetic, or as builder in vitamin tablets, among many others, is biologically and chemically inert; and is stable to photo- and chemical corrosion in addition to being inexpensive [Pelizzetti, 1995]. ZnO has similar mechanism of photodegradation and seems to be a suitable alternative to TiO_2 [Daneshvar et al., 2004]. The notable advantage of ZnO is that it absorbs over a larger fraction of solar spectrum than TiO_2. However, the important limitation of ZnO is its dissolution in acidic medium and therefore can be used only in alkaline pH. Other semiconductor particles (e.g., CdS or ZnS) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates, but unfortunately, such catalysts get degraded during the

repeated catalytic cycles. The band gap of various semiconductors is shown in Fig. 1.3.

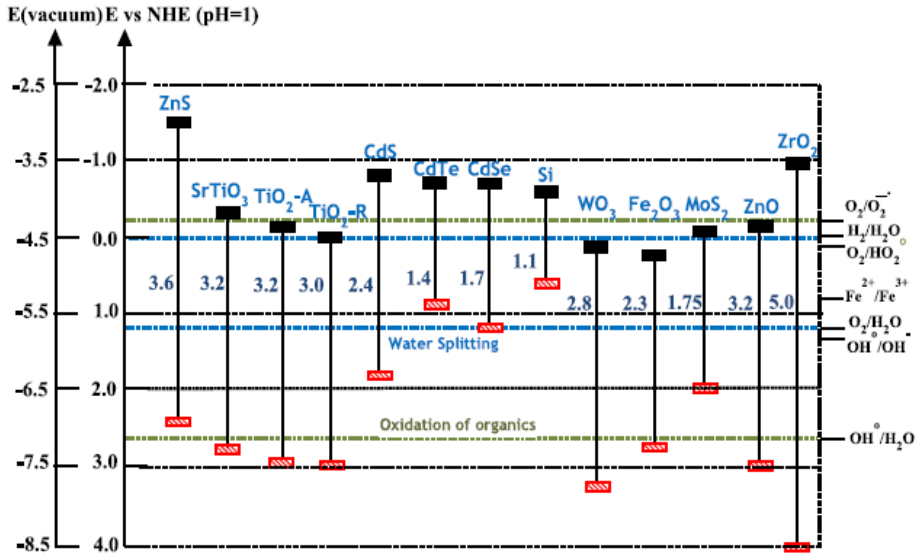


Fig.1.3 Band gap energy and band edge positions of different semiconductor oxides and chalcogenides (Source: Vinu and Madras, 2010)

1.4.3 Irradiation Sources

This electromagnetic spectrum present in space covers an extremely broad range, from radio wavelengths of a meter or more, down to x-rays with wavelengths of less than one billionth of a meter. The UV-visible region occupies an intermediate position, having both wave and particle properties in varying degrees. Visible light is concerned with the radiation perceived by the human eye having wavelength (λ) range of 400 to 770 nm. Short wavelength UV-light exhibits more quantum properties than its visible or infrared counterparts. According to its anecdotal effects, ultraviolet 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. UV-B (280-315 nm) is typically the most destructive form of UV light because it has enough energy to damage biological tissues and UV-C (100-280 nm) is almost completely absorbed in air within a few

hundred meters. Infrared range that spans 770 nm to 10^6 nm [1 (mm)] is responsible for an important part of the electromagnetic radiation that reaches the Earth. It is also divided into three types on the basis of wavelength viz. Infrared-A: 700 nm to 1,400 nm, Infrared-B: 1,400 nm to 3,000 nm and Infrared-C: 3,000 nm to 1 mm [kansal, 2006]. Of all the energy coming from sun, the earth receives 1.7×10^{14} kW [Hulstrom et al., 1985].

Solar ultraviolet radiation is only a very small part of the solar spectrum (between 3.5% to 8%). However this ratio may vary depending upon the geographical location and meteorological conditions. The percentage of global UV radiation (direct+diffused) generally increases when atmospheric transmissivity decreases mainly because of clouds, aerosols and dust etc.

1.4.4 Photoreactor

The reactors used for photocatalytic treatment are categorized as fixed-bed photoreactors and slurry batch photoreactors. According to various reports, mainly from laboratory scale investigations, slurry type reactors are presumably more efficient than those based on immobilized catalyst [Bideau et al., 1995; Chester et al., 1993; Matthews and McEvoy, 1992]. However for engineering applications, there is an intrinsic drawback to the first option; the need of a post radiation treatment of particle fluid separation, catalyst recycling and the ultimate goal of obtaining a clean, powder free water. Basically the solar photocatalytic reactors are of two types: Concentrating and Non-concentrating reactors. The first engineering–scale outdoor reactor for solar detoxification was developed by Sandia National Laboratories (USA) in late-eighties. Since then, many different concepts with a wide variety of designs have been proposed and developed all over the world, in a continuous effort to improve performance and to reduce the cost of solar detoxification system. Solar ponds can be constructed on-site, especially for wastewater treatment. Since industries

already use ponds for biological treatment of waste water, shallow solar ponds can be used for the front or back end of a coupled solar/biological treatment.

1.5 KINETICS

Chemical kinetics describes the studies of both the mechanism and rate of a chemical reaction [Smith, 1970; Hill, 1977]. Pseudo-first order reaction rate constants are determined via the same method as first-order reaction rate constants. The photocatalytic oxidation of most contaminants species via TiO_2 can be described with Langmuir-Hinshelwood kinetics [Matthews, 1990; Ollis and Truchi, 1990; Ku and Hsieh, 1992; Serra et al., 1994; Chang et al., 2000]. Langmuir–Hinshelwood kinetics utilize both reaction rate constant, k, and an adsorption equilibrium constant, K, to describe heterogeneous surface reaction [Hugul et al., 2002]. When the chemical concentration C_0 is millimolar solution (C_0 small), the equation can be simplified to an apparent first-order equation [Houas et al., 2001; Konstantinou and Albanis, 2003].

$$\ln(C_0 / C) = kKt = k_{app}t$$

or

$$C = C_0 e^{-k_{appt}t}$$

A plot of ln C_0/C versus time represents a straight line, the slope of which depends upon linear regression, equals the apparent first-order rate constant $k_{app.}$

1.6 COUPLING OF PHOTOCATALYSIS WITH BIOLOGICAL TREATMENT

Biological treatment of wastewater, groundwater, and aqueous hazardous wastes is often the most economical alternative when compared with other treatment options. Although some organic molecules are readily biodegradable, however, some of the synthetic and naturally occurring organic molecules are biorecalcitrant [Adams et al., 1994]. Methods for assessing biodegradability in these systems such as

BOD/COD or BOD/TOC have been proposed by a number of authors [Gilbert, 1987; Marco et al., 1997; Chamarro et al., 2001]. The most widely used biological treatment system at industrial scale is activated sludge process, which is also ineffective in complete removal of colour and toxicity of the effluents [Malaviya and Rathore, 2007], thus necessitating search and use of alternative treatment strategies. Although AOPs are cheaper than combustion or wet oxidation technologies, a serious drawback of AOP is their relatively high operational costs compared to those of biological treatments. Normally the wastewater that has COD value below (≤10 g/L) can be treated with AOP's, but if the quantity of COD is more, the necessary concentration of catalyst/oxidant increases, with negative effect on treatment cost. However, their use as both pretreatment step for the enhancement of the biodegradability of wastewater containing biorecalcitrant compounds [Parra et al., 2000, Sarria et al., 2002] or post biological step to remove the residual inhibitory organics can justify the cost implications to a significant extent. Therefore, coupling of AOP with inexpensive biological processes, can be used to achieve degradation of pollutants in a more economical and environment friendly manner.

In the last decade, intensive research is being carried out on application of coupled systems for treatment of wastewater generated by different industries [Takahashi et al., 1994; Ledakowicz and Gonera, 1999]. An improved system for treatment of effluent at industrial scale is envisaged to be solar photochemical process in tandem with an existing biological process that would not only achieve significant degradation of chloroorganics but also economize the energy and cost requirements. Keeping in view of these factors, the proposed study aimed at complete degradation of real bleach mill and combined pulp and paper mill effluents by integrating photocatalytic process along with conventional biological processes.

2.0 REVIEW OF LITERATURE

Wastewater generated from different industries is posing a great threat not only to mankind but also to the landmass fertility as well as natural flora and fauna. In recent times, very stringent regulations have forced researchers to explore and develop novel technologies to accomplish better quality of treated waters. The conventional separation mechanisms such as carbon adsorption, air stripping, coagulation, precipitation and flocculation magnify the risk of associated hazardous compounds and require further treatment of streams concentrated with contaminants [Hoffman et al., 1995; Jardim et al., 1997]. Based on the concentrations and the type of contaminants existing in the wastewater, various treatment methods have been developed to release an environmentally friendly effluent. The application of treatment method depends upon nature of the contaminants, their chemical structure, solubility, biodegradability, volatility, toxicity, polarity, oxidation potential, adsorbability, electrical charge, and the nature of degradation byproducts [Gogate and Pandit, 2004a; Gogate and Pandit, 2004b]. Different physical, chemical, and biological treatment processes have been employed to treat various municipal and industrial wastewaters such as food [Paraskeva and Diamadopoulos, 2006], pharmaceutical [Esplugas et al., 2007; Johnson and Mehrvar, 2008], pulp and paper [Moo-Young, 2007], dye processing and textile [Vandevivere et al., 1998; Aye et al., 2003; Aye et al., 2004; Crini, 2006] effluents. Biological treatment is the most widely used technique in the treatment of industrial wastewater due to its low initial and operational costs [Marco et al., 1997]. As an effective alternative, advanced oxidation processes (AOPs) have been experimented extensively to accomplish complete degradation of organic pollutants such as hydrocarbon fuels, halogenated solvents, explosives and their byproducts, phenols, aromatic carboxylic acids, aromatics,

aliphatic alcohols, microbes, surfactants and pesticides to mineralization products: mineral salts, carbon dioxide and water [Suri et al., 1993; EPA, 1998; Chang et al., 2000; Kansal, 2006].

2.1 BIOLOGICAL DEGRADATION

These processes are useful for treating biodegradable waste streams. The capital and operating costs of biological treatment methods are 5-20 and 3-10 times cheaper than those of chemical methods, respectively [Mamma et al., 2004; Mohan and Pittman, 2007]. Based on the cheaper capital investment and their operating cost, it is desirable to maximize the residence time and the removal rates of contaminants in biological processes. Biological treatments have certain drawbacks, such as the low reaction rate, difficult disposal of the activated sludge, the narrow range of pH and temperature for efficient biological treatment [Thompson et al., 2001; Parra et al., 2002]. Different types of biological approaches such as aerobic and anaerobic processes have been employed for treating pulp and paper mill effluents [Dangcong and Qiting, 1993; Chaudhry et al., 1999; Grover et al., 1999]. The aerobic processes are used more because of their efficiency and operational simplicity [Ruiz et al., 1992]. Biological treatment, generally by means of activated sludge [Wiesmann and Putnaerglis, 1986; Givens et al., 1991], in adequate conditions [Wu et al., 1994] has unquestionable advantages for the destruction of organic compounds. However, its application to the treatment of effluents having phenols, nitroaromatic, aliphatic compounds and industrial wastewater is restricted because of the high toxicity of these constituents. In addition, adjustment of pH to an adequate value, availability of carbon and oxygen in adequate quantities [González, 1993], becomes necessary since the efficacy of the process depends fundamentally on the viability and activity of the microrganisms [Urano and Kato, 1986; Kameya et al., 1995].

Anaerobic digestion is a process frequently employed for the secondary treatment of industrial wastewater [Pearson, 1990; Welander et al., 1999]. Typical COD removal data for the treatment of paper mill wastewater shows that a relatively constant removal efficiency of about 80% can be achieved. With fewer reports on degradation with anaerobic treatment [Clark et al., 1994; Nilsson and Strand, 1994; Fulthorpe and Allen, 1995], more work has been cited with aerobic cultures, particularly white rot fungi [Jokela et al., 1993; Imamura, 1995; Limura et al., 1996]. The anaerobic process also has an added advantage facilitating energy generation from methane. The main advantage of anaerobic treatment facility is to apply high loading rates i.e., 10 to 20 times higher than ASP. There have been few reports concerning the removal of adsorbable organic halides (AOX) in bleach effluent from pulp and paper mills via anaerobic means [Hakulinen and Salkinoja-Salonen, 1982; Hall and Cornacchio, 1988; Ferguson and Dalentoft, 1991]. Haggblon and Sakinoja-Salonen (1991) used a combination of aerobic and anaerobic treatments to achieve 65% AOX removal. In addition, Pallerla and Chambers (1996) and Bergbauer et al. (1991) reported AOX removal to the extent of 45-59% with *Trametes ersicolor*.

Biological degradation of chlorophenolic compounds have been carried out with white and brown rot fungi, such as *Trametes versicolor* and *Gloeophyllum striatum*, respectively [Zouari et al., 2002; Pedroza et al., 2007]. These fungi produce ligninolytic enzymes like laccase (benzenediol:oxygen oxireductase; EC 1.10.3.2) that catalyze the oxidation of a wide variety of organic and inorganic substrates with the simultaneous reduction of O_2 in water [Galhaup et al., 2002]. Black liquor and bleach effluent from an agro residue based pulp and paper mill were treated anaerobically to reduce their high COD contents and it has been reported that COD reduction is only 31-43% in 51 days whereas it was 66-73% with the addition of 1% w/v glucose in 38 days [Ali and Sreekrishnan, 2000]. The treatment of pulp and paper mill effluents by

different biological processes has been reviewed with the main focus on activated sludge process [Thompson et al., 2001].

Anaerobic pre-treatment turned out to be an effective way to multiply the BOD-treatment capacity by a factor of five, whereas the extra space required was only a small fraction (20 %) of what was required for a conventional expansion. In addition, the mills improved their total effluent plant operational cost and got rid of typical activated sludge plant problems like foaming and bulking. Because of the obvious advantages, today, more than 100 mills in the world apply a combination of anaerobic and aerobic treatment [Tsang et al., 2007].

2.2 ADVANCED OXIDATION PROCESSES (AOPs)

Due to the inability of biological treatments towards complete mineralization of industrial effluents, there is a need to focus on more efficient technology for the treatment of biorecalcitrant compounds present in the effluents. During the last two decades, fundamental and applied research in the field of AOPs has been performed extensively all over the world as documented by more than 2000 publications in various journals and proceedings [Blake, 2001]. Advanced oxidation processes (AOPs) have been suggested as potential degradation method especially for bio-refractory or toxic compounds [Khodja et al., 2001]. AOPs are an attractive alternative for the treatment of contaminated waters containing less biodegradable anthropogenic substances as well as for the purification and disinfection of drinking waters [Peyton et al., 1982; Glaze et al., 1987; Miller et al., 1988; Carey, 1990; Legrini et al., 1993; Masten and Davies, 1994; Benitez et al., 1995; Casero et al., 1997; Ulmann, 1998; Andreozzi et al., 1999]. Homogenous and heterogeneous AOPs have been employed for wastewater treatment by different research groups [Mansilla et al., 1997; Perez et al., 1997].

Homogeneous oxidation systems carry out the degradation of pollutants using H_2O_2/UV, H_2O_2/UV/O_3, UV/O_3 and photoassisted fenton degradation techniques [Vankatadari et al., 1993; Ho and Bolton, 1998; Alaton and Balcioglu, 2001; Shen and Wang, 2002]. However, these oxidation techniques for the degradation of organics are both cost and energy intensive. The heterogeneous photocatalytic systems (UV/semiconductors) have been extensively studied due to their ability to photosensitize the wide range of organic substrates at ambient temperatures and pressures, without the production of harmful by-products. The development of TiO_2 photocatalysts that can be utilized in solar or indoor artificial light for the degradation of pollutants is of great importance [Jansen and Letschert, 2000; Asahi et al., 2001; Ihara et al., 2001; Khan et al., 2002; Yu et al., 2002; Ihara et al., 2003; Sivalingam et al., 2003; Nagaveni et al., 2004a,b]. Degussa P-25 TiO_2 has been used for many systems either in suspended or in supported forms [Miller et al., 1999]. Many researchers have reported solar light to be useful UV source for driving photocatalytic processes [Barbeni et al., 1987; Matthews, 1987; Pacheco et al., 1991].

AOPs have high cost fundamentally due to high demand of electric energy either for ozonizers or for UV lamps. Application of solar irradiations to the photochemical process reduces cost but this is only possible for catalyzed heterogeneous reactions [Minero et al., 1993; Bockelmann et al., 1995; Blanco et al., 1996].

2.3 PHOTOCATALYSTS

The primary criteria for a good semiconductor photocatalyst for degradation of organic compound is that the redox potential of $^{\cdot}OH$ radical lies within the band gap domain of the material and it is stable over prolonged periods of time. Carey et al. (1976) first used the TiO_2 photocatalysed process for the dechlorination of polychlorinated biphenyls (PCB) in aqueous suspensions. A clear recognition and

implementation of semiconductor photocatalyst as a method of water purification was suggested by Ollis et al. (1983) who worked on photomineralization of halogenated hydrocarbon contaminants including trichloroethylene, dichloromethane, chloroform and carbon tetrachloride, sensitized by TiO_2.

Semiconductors (such as TiO_2, ZnO, Fe_2O_3, ZnS and CdS) can act as sensitizers for light induced redox processes due to the electronic structure of metal atoms in chemical combination, which is characterized by a filled valence band and an empty conduction band [Hoffman et al., 1995]. The most popular photocatalyst configuration on laboratory scale has been in the form of powder suspensions. Commercially available samples of TiO_2 (Degussa P-25, Millenium PC500, Aldrich, Hombikat UV 100, Tranox A-K-1, Mikroanatas IF 9308/18 and DuPont R-900) have been used in many studies [Rajeshwar et al., 2008]. Degussa P25 TiO_2 works the best for photoreactivity in environmental applications, although TiO_2 produced by Sachtleben, Germany show comparable reactivity [Martin et al., 1994]. Bouanimba et al. (2011) compared the efficiency of P25-Degussa and PC500-Millennium photocatalysts with higher efficiency of TiO_2 P25 towards degradation of Bromophenol blue. Degussa P25 TiO_2 has effectively become a research standard because it has (i) reasonably well defined nature (i.e. 70:30% anatase-to-rutile mixture with a BET surface area of 55±15 m^2/g, typically nonporous and crystallite sizes of 30 nm in 0.1 μm diameter aggregates and (ii) a substantially higher photocatalytic activity than most other readily available samples of TiO_2.

Hydroxyl radical ($OH^{\cdot}$) is the main oxidizing specimen responsible for photooxidation of the majority of the organic compounds studied. The first effect, after absorption of UV radiation, is the generation of electron/ hole pairs, which are separated between the conduction and valence bands. In order to avoid recombination of the pairs generated, if the dissolvent is oxidoreductively active (water) it also acts

as a donor and acceptor of electrons. In any case, it should be emphasized that even trapped electrons and holes can rapidly recombine on the surface of a particle. This can be partially avoided through the capture of electron by pre adsorbed molecular oxygen, forming a superoxide radical. Whatever the formation pathway, it is well known that O_2 and water are essential for photo oxidation with TiO_2, moreover, there is no degradation in the absence of either [Kansal et al., 2006].

The TiO_2 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 [Hoffmann, 1995; Mills and Hunte, 1997; Litter, 1999]. Martin et al. (1994) and Mills et al. (1993a & b) claim that rutile TiO_2 is catalytically inactive whereas Karakitsou and Verykios (1993); Ohtani and Nishimoto, (1993) reported it's lesser or selective activity. The anatase form of titania is reported to give the best combination of photoactivity and photo stability [Zeltner and Tompkin, 2005]. 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. The VB and CB energies of the anatase TiO_2 are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and therefore absorbs in the near UV light (<387 nm). While in case of rutile phase, the band gap is 3.0 eV. Anatase is thermodynamically less stable than rutile, but its formation is kinetically favoured at lower temperature (<600^oC), which could explain its higher surface area, and higher surface density of active sites for adsorption and for catalysis. It is produced through high-temperature (greater than 1200^oC) flame hydrolysis of $TiCl_4$ in the presence of hydrogen and oxygen. The TiO_2 so formed, is treated with steam to remove HCl which is also produced as part of the reaction. The product is 99.5% pure TiO_2 (anatase : rutile ratio, 70:30), which is non-porous, with

rounded edges cubic particles. The P-25 TiO_2 powder has a surface area of 50 m^2/g and an average particle diameter of 21 nm. 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 photoefficiency [Sun and Smirniotis, 2003]. The XRD pattern of TiO_2 (P-25) shows peaks corresponding to anatase and rutile phases. The XRD peak of crystal plane 101 for anatase appeared at 25.4 (2θ) and crystal plane 110 for rutile at 27.5 (2θ) indicated that TiO_2 (P-25) contains on average 85% anatase and 15% rutile phases.TiO_2 (P-25) has very small average particle size (1.25 μm) with large surface area (50.46 m^2/g) [Sakthivel et al., 2003]. SEM micrograph of commercial TiO_2 from Degussa consists of agglomerates of particles in the nanometer size, very difficult to separate from the aqueous solution [Aguado et al., 2002].

Although TiO_2 in the anatase form has been used for many environmental applications rather extensively, attempts have also been made to study photocatalytic activity of other semiconductors such as SnO_2, ZrO_2, CdS, MoS_2, Fe_2O_3, WO_3 and ZnO [Konstantinou et al., 2002]. Studies included observations on ZnO [Ohnishi et al., 1989], CdS [Reutergardh and Iangphasuk, 1997], FeO and ZnO [Agarwal et al., 2002] and WO_3 [Poulios and Tsachpinis, 1999]. Bhatkhande et al. (2001) reviewed the work of various research groups on diverse variety of compounds degraded by photocatalysis. Amongst the various catalysts examined so far, ZnO (3.2 eV) has been reported to be a suitable alternative to TiO_2 as far as band gap energy is concerned. The quantum efficiency as well as the photocatalytic efficiencies of ZnO powder is also significantly larger than that of TiO_2 powder [Richard et al., 1992; Tennakone et al., 1992]. The important advantage of ZnO is its potential to absorb over a larger fraction of solar spectrum than TiO_2 [Sakthivel et al., 2003]. Therefore, ZnO photocatalyst can be considered most suitable for photocatalytic degradation in the presence of sunlight.

Kansal et al. (2008) investigated the photocatalytic degradation of lignin in the presence of ZnO photocatalyst both in the slurry and immobilized form using a coated film photoreactor under solar irradiation and indicated that ZnO was reported to be better photocatalyst than TiO_2. The effects of parameters like catalyst loading, initial substrate concentration, UV irradiation intensity and pH on the extent of photodegradation have been investigated. Studies have also been done using ZnO catalysts under sunlight [Neppolian et al., 1998; Chakrabarti and Dutta, 2004] with promising results from ZnO nanoparticles than that of the ZnO nano-crystalline particles. Several authors apply varying design of experiments for discolouration of wastewater [Herrera et al., 2000; Lizma et al., 2002 and Muthukumar et al., 2004]. Karunakaran et al. (2010) also reported importance of ZnO as a suitable alternative to TiO_2 for degradation of cyanide under similar conditions.

The metal sulphide semiconductors such as CdS are unsuitable based on the stability requirements in that they readily undergo photoanodic corrosion, while iron oxides are not suitable semiconductors, as they readily undergo photocatalytic corrosion and this property renders it unacceptable as a photocatalyst for water purification [Karunakaran and Senthivelon, 2005] even though they are inexpensive and have nominally high band gap energies.

2.4 MIXED PHOTOCATALYSTS

Coupling/doping of transition metal for the modification of the semiconductor can be employed in order to increase its photocatalytic activity, use in solar irradiation and industrial recovery [Anpo et al., 2000; Chen et al., 2005]. The synthesis of nanostructured TiO_2 has been reported in several studies, where the modified catalyst has higher activity compared to that of Degussa P-25 in degrading pollutants both under UV exposure and with solar irradiation. The reason for the higher activity was

attributed to the higher hydroxyl ion content on the catalyst surface and crystallinity extended till the surface with reduced band gap [Sivalingam et al., 2003; Nagaveni et al., 2004b]. The influence of dissolved transition metal impurity ions on the photocatalytic properties of TiO_2 has become another interesting area of semiconductor modification. Paola et al. (2002) reported that photocatalytic activities of TiO_2 polycrystalline powders loaded with transition metals, such as Cr, Co, Cu, Fe, Mo, W and V, are generally reduced due to the presence of the transition metals. The major practices involve catalyst modification by doping, metal coating, surface sensitization, and increase in surface area by design and development of secondary titania photocatalyst. Surface sensitization has been extensively reviewed by Carp et al. (2004).

Instead of using TiO_2 alone, a "coupled/mixed semiconductor" configuration [Tacconi et al., 2003] improves charge separation in many cases because of "vectorial" electron transfer [Smotkin et al., 1986]. The performance of various composites formed by TiO_2 and other inorganic oxides or sulfides has been reported [Jiang et al., 2008]. The p-ZnO/TiO_2 was prepared by ball milling of TiO_2 in H_2O solution doped with p-ZnO and its photocatalytic activity for oxidation of methyl orange was reported [Shifu et al., 2008]. Nanosized coupled ZnO/SnO_2 photocatalysts with different Sn contents were prepared using the coprecipitation method and enhanced photocatalytic activity of the coupled ZnO/SnO_2 photocatalyst was reported as compared to ZnO and SnO_2 by Wang et al. (2004). Liu et al. (2010) prepared mesoporous ZnO/SnO_2 composite nanofibers via the electrospinning technique and found that the photocatalytic activity of the mesoporous ZnO/SnO_2 composite nanofibers was dependant on the surface area, light utilization efficiency, and the separation of photogenerated electron/hole pair. TiO_2/SnO_2 photocatalyst prepared by ball milling through doping of TiO_2 using H_2O as disperser showed new crystal faces

with no change in crystal faces of TiO_2 [Shifu et al., 2006]. Korosi et al. (2004) prepared SnO_2/clay nanocomposites having Sn content varying between 15 and 50 percent by weight. The photooxidative efficiency of SnO_2/clay photocatalysts was investigated and established that the catalytic effect is mainly due to the presence of nanosized tin dioxide particles. Bessekhouad et al. (2006) investigated the activity of TiO_2, CdS and coupled CdS/TiO_2 powders and concluded that under visible light, CdS/TiO_2 exhibit faster degradation rate than either of the photocatalysts. Other studies report "coupled" semiconductor powders (TiO_2/ZnO, TiO_2/SnO_2, ZnO/ SnO_2) [Wu, 2004; Wu and Chang, 2006] but it is not clear whether the two semiconductor particles are truly coupled in majority of the cases.

2.5 DEGRADATION OF CHLORINATED ORGANICS

Organic compounds present in environment are of major concern due to their toxicity and non-biodegradable nature. The paper and pesticides industries are the main sources of wastewater with chlorophenols [Fukushima and Tatsumi, 2001; Bao-xiu et al., 2007]. The pulp bleaching effluents contain about 85% of low molecular weight organic compounds such as acidic, phenolic and chlorinated organics [Jokela and Salkinoja-Salonen, 1992; Savant et al., 2006; Kreetachat et al., 2007]. Phenolic organics such as chlorophenols and chlorocatechols are dominantly present in wastewater generated from pulp and paper mills, tanning, petroleum refining, etc. [Kansal et al., 2008]. The bleaching effluent is considered to be the most polluted due to presence of about 500 different chlorinated organic compounds including chlorinated hydrocarbons, phenols, catechols, guaiacols, syringols, furans, dioxins, chloroform, chlorate, resin acids etc. [Sunito et al. 1988; Freire et al. 2003]. Chlorophenolic compounds are recalcitrant to biodegradation and therefore persistent in the environment. Because of their lipophilicity they can transport through the cell

membrane and bio-accumulate in aquatic organisms [Pedroza et al., 2007]. Most of plants are very sensitive to the phytotoxicity of chlorocompounds. Such compounds may be present in the aquatic environment in many forms such as dissolved, free or complexed form, adsorbed on suspended inert solid or benthic sediments, or carried in biological tissues. They are considered harmful for human health due to their potential carcinogenic as well as mutagenic activity and are listed by USA EPA as priority environmental pollutants [EPA, 1988]. Chloroguaiacols have adverse environmental impacts necessitating their treatment before release into environment [Samet et al., 2002).

Biological treatment for the decomposition of many chlorinated phenols have been found to be inefficient since chlorinated phenols are resistant to biodegradation in an acceptable time period and tend to accumulate in sediments [Pitter and Chudoba, 1990; Howard, 1991; Crompton, 1997]. Biodegradation of chlorinated guaiacols (4-chloroguaiacol, 5-chloroguaiacol and 4,5-dichloroguaiacol) was studied using guaiacol-degrading *Acinetobacter junii* strain [Gonzalez et al., 1993]. This bacterial strain has ability to use guaiacol as the sole carbon and energy source and effectively degraded 4,5-dichloroguaiacol. The metabolism of chloroguaiacols was also studied in *Rhodococcus chlorophenolicus* and *Rhodococcus tuber* CA16 [Haggblom et al., 1986; Claudia et al., 1995]. Chlorophenols do not undergo photolysis under direct sunlight in the natural environment since they absorb light below 290 nm [Ollis and AI-Ekabi, 1993]. Alternative methods to conventional pollutant destructive technologies involve oxidation of chlorophenols with reagents such as air or oxygen in wet oxidation and superficial wet oxidation [Li et al., 1991; Lin et al., 1998; Lee et al., 2002], electrons in electrochemical oxidation [Comninellis, 1994; Rodgers et al., 1999], potassium permanganate, chlorine, hydrogen peroxide and ozone [Yin and Allen, 1999]. Barbeni et al. (1985) performed the photodegradation of

pentachlorophenol sensitized by use of different semiconductors (such as TiO_2, ZnO, CdS, WO_3 and SnO_2) and found TiO_2 to be the most active among all the different semiconductor photocatalysts. Several investigations of photocatalytic decomposition of chlorophenols using semiconductor either in aqueous heterogeneous suspension [Al-sayyed et al., 1991; Stafford et al., 1994; Serpone et al., 2000; Axelsson and Dunne, 2001] or in an immobilized form [Al-Ekabi et al., 1989; Vinodgopal et al., 1992] have been published. Most bench scale UV/TiO_2 systems utilize suspensions of TiO_2 particles and are operated in batch mode [Hoffmann et al., 1995; Jardim et al., 1997; Almquist et al., 2003]. The investigations on the photocatalytic oxidation of phenol and chlorophenols in the presence of ZnO as photocatalyst revealed better degradation efficacy [Lathasree et al., 2004].

The degradation of guaiacol and syringol has been observed to be effective using Fenton reagent, which is found to have beneficial effect on total organic carbon (TOC) decay rate [Perez et al., 2002]. Eugenol and guaiacol has also been efficiently degraded by employing solar photocatalysis [Amat et al., 2005]. The chlorophenols, chlorocatechols, and chloroguaiacols are of increasing environmental interest because of their formation during pulp bleaching [Hossain et al., 2001; Jayaramraja et al., 2001; Chaudhary et al., 2002; Pokhrel and Viraraghavan, 2004]. Together, they account for 47 % of the low molecular weight chlorinated material produced per ton of kraft softwood pulp [Kringstad and Lindstrom, 1984]. Chlorocatechols and chloroguaiacols are priority pollutants under USEPA due to their acute toxicity and recalcitant nature [EPA, 1988]. Substituted catechols, especially chlorinated and methylated catechols, are by products in pulp and oil mills [Neilson et al., 1991; Capasso et al.,1995]. Kessalman et al. (1997) investigated the photoelectrochemical degradation of 4-chlorocatechol at TiO_2 electrodes focusing on: comparison between sorption and photoreactivity. Li et al. (1999) have studied the TiO_2-mediated

photocatalytic degradation of 4-chlorocatechol as a reaction intermediate formed during the degradation of 4-chlorophenol and a degradation pathway of 4-chlorocatechol (4-CC) has been suggested.

The literature study reflects that there has been limited focus on the degradation of chloroguaiacols with few studies limited to electrochemical oxidation and wet catalytic oxidation employing different composite oxide to remove 4-chloroguaiacol from softwood pulp mill effluents [Hamoudi et al., 2001; Samet et al., 2002]. The TiO_2-photocatalysed degradation of phenol and ortho-substituted phenolic compounds using aqueous solutions of phenol, guaiacol, 2-chlorophenol and catechol revealed that Langmuir-Hinshelwood kinetics for the degradation of each one of the phenolic compounds is obeyed [Peiro et al., 2001]. Parametric optimization of photocatalytic degradation of catechol in aqueous solutions by response surface methodology has also been reported [kansal et.al., 2007]. The photocatalytic degradation of 2,4-dichlorophenol in irradiated ZnO suspension has been reported [Abdullah et al.,2010].

2.6 PHOTOCATALYTIC DEGRADATION OF PULP AND PAPER MILL FFLUENTS

The consistently increasing demand for paper products and limited availability of forest based raw materials has forced to use alternate non-woody/ agro-residues raw materials such as wheat straw, rice straw, bagasse, sarkanda, jute, cotton stalks etc. which are abundantly available in an agrarian country like India. As a general practice, wheat straw is washed prior to its use in pulping because of high chloride content that can create problem in black liquor recovery resulting in generation of wet washing effluent. The soda process is one of the most popular methods in the pulp and paper industry to obtain cellulosic pulps. Effluent of pulp mill is highly polluted, and characterized by parameters unique to this waste water such as colour, absorbable

organic halides (AOX) and related organic compounds [Fitzsimans and Eriksson, 1989; Elisa et al., 1991]. Bleaching is usually carried out using chlorine and chlorine dioxide and the products are solublized by extraction with NaOH. The alkaline extraction stage of bleach plant effluent is a major source of colour and is mainly due to the presence of lignin and its derivatives. Lignin is a heterogeneous, three dimensional polymer, composed of oxyphenylpropane units. Lignin wastewater is discharged from the pulping, bleaching and chemical recovery section. The high chlorine content of bleach plant react with lignin and its derivatives to form highly toxic as well as recalcitrant compounds which are responsible for high biochemical and chemical oxygen demand. The compounds present in the chlorination (C) and caustic extraction (E) effluents are mainly chlorophenolics, resin and fatty acids. Sharma et al. (1996a) analyzed the laboratory generated bleach liquor from the C and E stages of bagasse and wheat straw pulps qualitatively and quantitatively for various chlorophenolics, resin and fatty acids using gas chromatography and identified number of chlorinated derivatives of phenols, catechols, guaiacols, syringaldehydes, resin acids as well as unchlorinated saturated and unsaturated fatty and resin acids. Later similar GC-MS studies were conducted on kahi grass [Sharma et al., 1996(b)], bamboo [Sharma et al., 1997] and rice straw pulp [Sharma and Kumar, 1999].

The effluent produced is considered to be of serious hazard due to chemical diversity of impurities present as well as complexity of chemical structures [Bajpai 2000; Pokhrel and Viraraghavan 2004]. The high chemical diversity of these pollutants cause a variety of clastogenic, carcinogenic, immunological and mutagenic effects on fishes and other aquatic communities in recipient water bodies [Schnell et al., 2000; Rana et al., 2004].

Several methods have been attempted for the removal of colour from the pulp and paper mill effluents. The biological colour removal process is particularly

attractive since in addition to colour and COD, it also reduces BOD and low molecular weight chlorolignins [Nagarthnamma et al., 1999]. Partial decolourization was achieved while treating pulp bleach effluents using hydrogen peroxide in combination with UV light [Prat et al., 1988]. Kumar et al. (2011) studied the colour removal from kraft pulp bleaching wastewater using heterogeneous photocatalysis. Physical and chemical processes are quite expensive and remove high molecular weight chlorinated lignins, colour, toxicants, suspended solids and chemical oxygen demand, but BOD and low molecular weight compound are not removed efficiently [Singh and Singh, 2004].

A comparative study of homogeneous and heterogeneous advanced oxidation processes for the treatment of bleaching effluent of pulp and paper industry has been reported and heterogeneous processes have been found to be more effective in the removal of chlorinated organics from the effluent [Mansilla et al., 1997]. Villasenor and Mansilla (1996) studied the ZnO-photocatalyzed reaction of kraft black liquor to determine the kinetic parameters and the mineralization reactions that exhibited first order dependence on the concentration of the substrate at 25^0C. Peralta-Zamora et al. (1998) reported the treatment of effluent from the cellulose and textile industries by applying heterogeneous photocatalytic procedure using UV light and free or matrix-supported immobilized catalyst. Evaluation of ZnO, TiO_2 and supported ZnO on the photoassisted remediation of different effluents was done in order to compare the applicability of heterogeneous photocatalytic systems. Tanaka et al. (1999) studied the photocatalytic degradation of lignin and found that carbohydrate aldehydes formed as intermediates. Yeber et al. (1999) studied the degradation of a pulp mill ECF bleaching effluent by several advanced oxidation reactions. When the effluent was subjected to ozonation and other advanced oxidation treatments (O_3/UV, O_3/UV/ZnO, O_3/UV/TiO_2, O_2/UV/ZnO, O_2/UV/TiO_2), the biodegradability increased significantly.

Lanzalunga and Bietti (2000) discussed the basic mechanistic aspects of the photo and radiation chemistry of lignin model compounds (LMCs) with respect to important processes related to lignin degradation. The use of different catalysts including TiO_2 and ZnO supported on raschig rings has been reported and their comparative studies were done. The advantage of immobilized catalyst and the possibility to use these systems under flow conditions has been discussed [Yeber et al., 2000]. The study of different intermediates produced during the photo catalytic treatment of bleach mill effluent was done using GC-MS technique and reported the presence of various chlorinated phenolics alongwith their concentrations [Ormad et al., 2001]. Torrades et al. (2001) found synergistic effect of simultaneous photocatalysis and ozonation to be more advantageous for destroying organic contaminants in bleached kraft mill effluent. Perez et al. (2001) evaluated the TiO_2-photocatalytic degradation of a cellulose ECF effluent using multivariate experimental design. The pH, catalyst amount and H_2O_2 were simultaneously varied using multivariate analysis to establish the weight of each variable in reduction of adsorbable organic halides (AOX) to 95%, total organic carbon (TOC) to 50%, total phenols and toxicity from the bleaching effluent.

Kisibi et al. (2003) have optimized the conditions for the photocatalytic degradation (UV/TiO_2) of lignin present in mill effluents from pulp and paper industries. It was seen that intermediate products obtained during degradation could be isolated and used as valuable industrial products. Machado et al. (2003) studied the use of photocatalysis to degrade the organic matter present in the effluent from a paper and cellulose mill. The best conditions for the photocatalytic process at a laboratory scale were determined using real effluents and an aqueous solution of a pregraded lignosulfonate as model compound for large scale studies. Results showed that the reaction was little influenced by temperature. On the other hand, parameters

such as pH, the use of some additives and morphology of the photocatalyst exerted a considerable influence on the results. The best conditions were tested under solar irradiations using compound parabolic collectors (CPC) set up for large volumes of effluent.

Boyd and Almquist (2004) studied the feasibility of photocatalytic method for the treatment of paper mill wastewater and stated that low concentrated wastewater could be easily fully degraded while highly concentrated effluent could be partially degraded. It has been shown that the rates of chemical oxygen demand (COD) removal from the wastewaters follow first order kinetics at low initial COD concentrations (increase with increasing COD concentrations) and then become zero order kinetics at higher COD concentration (a constant rate of degradation). Sattler et al. (2004) discussed the solar photocatalytic system for the degradation of lignosulfonate and the real effluent and reported that non-biodegradable substances could be effectively degraded by photocatalytic treatment, especially using CPC type reactor, resulting in fast degradation and total mineralization of the contaminants. Moiseev et al. (2004) studied the influence of photocatalytic process parameters like pH, TiO_2-modification, TiO_2-concentration, catalyst re-use and concentration of compound on the process efficiency. Increase in BOD_5/TOC ratio after a short irradiation period indicated that the use of photocatalytic oxidation as a pretreatment step for the enhancement of the biodegradability of wastewater. Caliman and Balasanian (2005), after conducting a survey in the field of photocatalytic reactors reported the major issues that should be considered for the development of commercially available photocatalytic systems for different purposes: use of suspended or supported catalysts and of concentrated or non concentrated sunlight. The common problems encountered in the design of photocatalytic reactors were also discussed and a few modalities for increasing their performances were proposed.

Studies have been reported on the simultaneous use of TiO_2 with H_2O_2 as well as TiO_2 coupled with Fenton and ozonation with UV light to degrade the organic carbon from the bleach mill effluent [Agustina et al., 2005]. The use of solar light in compound parabolic collectors rather than UV light was demonstrated by various authors for the detoxification of pulp and paper mill effluents [Sattler et al., 2004; Blanco-Galvez et al., 2007]. The life cycle assessment of different AOP's show that heterogeneous photocatalytic coupled with the Fenton's reagent reduce the adverse impacts on the environment due to significant TOC reduction [Munoz et al., 2006]. The possibility of degradation of various constituents of bleaching effluent in a photochemical treatment in the presence of semi conductor such as TiO_2, ZnO, WO_3 has been previously reported [Ebru and Fikret, 2008]. Kansal et al. (2008) reported the degradation of wastewater generated from kraft and soda pulping from agro-residue based paper mills using a heterogeneous photocatalytic system and the results reveal that photocatalytic degradation is an effective method in the degradation of biorecalcitrant pulp and paper mill effluents. Kumar et al. (2011) carried out the optimization of process parameters for the photocatalytic treatment of paper mill wastewater.

2.7 COUPLED TREATMENT

The treatment of pulp and paper mill effluents has been carried out by conventional processes involving physical, chemical, electrochemical and biological methods. Nevertheless, these techniques applied individually are generally limited and cannot completely degrade recalcitrant organic matter [Ali and Sreekrishnan 2000; Thompson et al. 2001]. Biological processes such as anaerobic and aerobic systems are used to treat pulp mill effluents but these have limited ability to metabolize lignin because of their size and complex structure [Balcioglu et al. 2007; Silva et al. 2007].

Biological treatment systems such as activated sludge process (ASP) are the most preferred processes in effluent treatment protocols of pulp and paper mills due to their commercial viability. However, due to the ineffective removal of color and toxicity of the effluents through biological treatment, the treated wastewaters are generally not recycled back to the industrial processes.

Efforts have been made in the past on using anaerobic/aerobic sequence processes for degradation of toxic compounds, mainly chloro-organics. Sequential environments are sometimes the best alternative to the detoxification of organic compounds. Aerobic and anaerobic environments each have limitations in their biodegrading abilities that often complement each other when they are combined. Most highly chlorinated chemicals, which are appreciably degraded under anaerobic conditions, are refractory to conventional aerobic conditions. Some authors have found that' common aerobic microorganisms could not degrade highly chlorinated aromatic substrates, such as hexachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,4-trichlorobenzene [Zitomer and Speece, 1993], or heterosubstituted aromatics, such ,as 4-chloro-2-nitrophenol (CNP) [Beunink and Rehm, 1990]. In contrast, investigations done over the past few years have indicated that biologically mediated dehalogenation of highly chlorinated compounds occurs under reduced, anaerobic conditions. The first steps of reductive dehalogenation are the successive removal of the halogens, leading immediately to the formation of less halogenated products that are less toxic and more amenable to further aerobic mineralization [Horowitz et al., 1983; Mohn and Tiedje, 1992]. The more halogenated a compound is, the faster the dehalogenation reaction [Vogel et al., 1987]. Pentachlorophenol (PCP) has been shown to be completely mineralized in both aerobic and anaerobic systems provided they have high biomass retention time and a long acclimation period. Aerobic fluidized beds were able to completely mineralize a mixture of chlorophenols (CP) [Puhakka and

Järvinen, 1992]. However, in other cases of anaerobic treatment within UASB and anaerobic filter reactors, complete mineralization of PCP did not occur; PCP was transformed in less chlorinated phenols, such as TeCP, 3,4,5-TCP, 2,4,6-TCP, 2,4,5-TCP, 3,4-dichlorophenol and 3- or 4-chlorophenol, with methanol, acetate, phenol and/or glucose as co-substrate [Woods et al.,1989; Hendriksen and Ahring, 1992]. Yet, these homologs could be brought to an aerobic system and completely mineralized without limitation [Armenante et al., 1992].

Chen and Horan (1998) have reported the use of a two stage anaerobic-aerobic approach to remove COD and sulphate from the wastewater generated in an integrated news print mill. The COD and sulphur removal achieved were 66% and 73% respectively. In general, anaerobic digestion is carried out at mesophilic temperatures, 35-37^{o}C. However the use of the thermophilic temperature range is worth considering as it will give faster reaction rates and higher gas production rate [Rintala et al., 1991; Fujian et al., 2001]. Welander et al. (1999) obtained high removal of chemical oxygen demand (COD) using anaerobic followed by aerobic biological treatment at 55^{o}C. Although anaerobic treatment showed a better operating economy, it was more sensitive to inhibitory compounds. Ferguson and Dalentoft (1991) attempted degradation in terms of adsorbable organic halides (AOX) by combining anaerobic and aerobic treatments. There was 30– 35 and 40–45% AOX reduction by aerobic and anaerobic methods independently wherein with the combination of the two processes, AOX reduction was about 50–55%. However, it is important to note that the majority of these studies involve utilization of highly specialized dechlorinating microbes, grown in optimum sterilized conditions in the presence of enriched medium [Pallerla and Chambers, 1996]. The economic viability of adopting such a strategy for treatment of a waste stream is highly questionable. Moreover, despite employing such

‘ideal condition’ based approaches, degradation rates have not been shown to be significantly high, peaking at 60% on an average.

In most of the above cases, anaerobic transformation is thus incomplete, and less chlorinated aliphatics or aromatics are the end products of the anaerobic processes. In contrast, aerobic microorganisms are efficient degraders of less chlorinated organic compounds up to complete mineralization. Anaerobic digestion is thus indicated as a primary treatment step to convey less chlorinated or dechlorinated compounds-containing effluents to an aerobic polishing unit. In the above treatment schemes, the anaerobic and aerobic bacteria operate in separate units that complement each other. Despite its great potential, the anaerobic/aerobic sequence might not be the optimal arrangement. In some cases, anaerobic partial degradation results in products which are just as or more toxic than the primary molecules. These products can accumulate in the anaerobic stage where they could inhibit anaerobic microorganisms themselves prior to being released in to the subsequent aerobic unit. This might decrease the effectiveness of the overall system from a certain feeding level. One economical scheme may be a single bacterial culture unit exposed to a cyclic anaerobic-aerobic sequence. Knowledge on these operations is still limited.

Advanced oxidation processes (AOPs) could be desirable alternative to treat and eliminate biorecalcitrant compound present in bleach mill effluents. The most eye-catching drawback of advanced oxidation technologies is their operating cost compared to other conventional physicochemical or biological treatments due to use of UV light and long retention time for the removal of the recalcitrant molecules. As these processes are relatively expensive when compared to conventional biological treatment, biological treatment is considered to be among the best available technologies (BAT) for wastewater treatment [Sarria et al., 2002]. However, the retention of toxic, stable and recalcitrant pollutants in biological processes

necessitates intervention of advanced oxidation processes. Therefore, the combination of AOP with biotreatment seems to be an economic and effective option. This integration is justified commercially when intermediates are easily degradable in the next process. Such an integrated approach of AOP and biological treatment has been reviewed by Scott and Ollis (1995) and Kang and Hoffmann (1998). Birnie et al. (2006) reviewed the existing photocatalytic reactors used in research and commercial applications and the guiding principles of effective reactor design were also discussed.

AOPs are also able to enhance the biodegradability of contaminants through converting recalcitrant contaminants into smaller and consequently more biodegradable intermediates. Several authors have augmented the applications of AOP's to degrade the pulp mill bleaching effluent and it has reflected from their study that biodegradability increased significantly after photocatalytic treatment [Yeber et al., 1999]. Ozone and UV system appears to be the most efficient in transforming the organic matter to more biodegradable forms. Combined photochemical treatment employing ZnO supported on sand and enzymatic treatment has been shown to be effective in the decolourization of the Kraft E1 effluent [Reyes et al., 1998]. Balcioglu and Cecen (1999) studied the biological treatability and TiO_2 photocatalysed oxidation characteristics of sulfate pulp bleach effluents and suggested the introduction of biological treatment step before the photocatalytic oxidation system. Pedroza et al. (2007) reported the degradation of chlorophenol from bleaching process during paper production by sequential biological-AOP using *T. versicolor* and UV/TiO_2/RuxSey obtaining a 99% chlorophenol removal after 96 h and 20 min with a 97% reduction in chemical oxygen demand (from 59 g/L). Tamer et al. (2007) evaluated the degradation of a mixture of chlorophenols by sequential AOP-biological process using activated sludge and either UV, $UV/TiO_2/H_2O_2$, UV/TiO_2 or UV/H_2O_2 as oxidant agent. Karimi et al. (2010) reported that the efficiency of advanced

oxidation processes (AOPs), enzymatic treatment and combined enzymatic/AOP sequences for the colour remediation of soda and chemi-mechanical pulp and paper mill effluent. It was found that both versatile peroxidase (VP) from *Bjerkandera adusta* and laccase from *T. versicolor*, as pure enzymes, decolorize the deep brown effluent to a clear light-yellow solution. Kumar et al. (2011) investigated the advanced photocatalytic oxidation of the pulp and paper industry effluent (primary clarified and biotreated) with UV/TiO_2 and UV/TiO_2/H_2O_2 treatment processes for environmental load reduction. Addition of hydrogen peroxide to the UV/TiO_2 system enhances the photoprocess performance. Higher COD, BOD, and color reduction is obtained for biotreated effluent as compared to primary clarified one.

Thus, these coupled processes emerge to have the capability of significant degradation and partial mineralization of the industrial effluents [Perez et al., 2002; Assalin et al., 2004; Momani et al., 2010]. Some latest investigations on the coupling of advanced oxidation followed by biological treatment or vice versa has been carried out to improve removal efficiencies and reduce process energy cost [Sarria et al., 2002; Tabrizi and Mehrvar, 2004; Battimelli et al., 2010]. When working with coupled AOP and biological processes, some practical aspects must be taken into consideration. On the one hand, chemicals and bioculture cannot mix because the chemicals used can cause damaging effects to the microorganisms. In addition, there may be detrimental effects by an excessively acidic or alkaline pH, necessitating pH adjustment to near neutral level. Large retention time in AOPs is not necessary when coupling both treatments but resulting final effluent from the phototreatment should be free from toxic and biorecalcitrant compounds. In this way, the assessment of biodegradability is necessary to determine an optimum pretreatment time that guarantees the success of the coupled system.

The sequencing of integrated treatment depends upon the biodegradability of wastewater because the readily biodegradable wastewater must be pretreated with biological treatment. This aspect is interesting from an economic point of view, since the costs of operation of a biological process is much smaller [Scott and Ollis, 1995; Marco et al., 1997]. For hardy biodegradable wastewater there are two alternatives and the selection of any of these alternatives depends on wastewater characteristics. Wastewater that contains high level of organic matter can be diverted first to biological treatment to eliminate all the biodegradable compound and then to chemical process. In second stage involving chemical process biorecalcitrant waste can be totally minerlized or it can be oxidized into smaller by-products that are more biodegradable so that the effluent can be recycled to biological process to complete the treatment process. With respect to non-biodegradable wastewater, a potentially viable solution is the integration of AOP and biological treatment processes [Gilbert, 1987; Marco et al., 1997; Beltrán et al., 2000]. Therefore, the integration of two processes namely photocatalysis under solar mode and biological systems can be the most effective and economical technology [Parra et al., 2000]. In the first process the toxic and/or non-biodegradable compounds would be eliminated until the point where inhibition no longer exists due to their toxicity. Subsequently, mineralization can be achieved in an easier and shorter time with the biological treatment [Sarria et al., 2002].

Another approach involving application of ozonation at the end of the industrial treatment line, after biological and physico-chemical stages, achieves an important removal of the residual organic matter in the effluent. The biodegradability enhancement resulting from partial oxidation of paper mill effluents allows an appropriate sequencing of ozonation followed by biofiltrattion, so that the combined oxidation process provides high COD elimination efficiency together with a reduced

ozone need [Baig, 2001]. Moraes et al. (2006) applied combined AOP (photocatalysis or ozonation) and biological process for treating Kraft E1 and black liquor effluent. Suspended photocatalysis showed a better decolorization for Kraft E1 with respect to ozonation. On the other hand, decolorization of black liquor effluent was more desirable with ozonation due to the darkness of the solution. Photocatalysis showed 45% improvement in mineralization of Kraft E1, but ozonation enhanced 37% mineralization in combined method. Bijan and Mohseni [2005] showed that ozone treatment enhanced the biodegradability of the effluent (from a pulp mill alkaline bleach plant effluent) allowing for a higher removal of pollutants. The conversion of high molecular weight (HMW) to low molecular weight (LMW) compounds was an important factor in the overall biodegradability enhancement of the alkaline effluent.

Balcioglu et al. (2007) reported the merits of combined ozonation and catalytic ozonation pre-treatment in the algal treatment of pulp and paper mill effluents Biological processes such as activated sludge and aerated lagoons have limited ability to metabolize lignin because of their size and complex structure. Tunay et al. 2008 studied the degradation of 2 different effluent samples with 2500 and 3520 mg/L COD, which were chemically treated with alum, lime and polyelecetrolyte up to 1900 mg/L, followed by activated sludge process up to 260-400 mg/L, then secondary wastewater was treated by ozonation, catalytic ozonation, H_2O_2/O_3, and Fenton. The treatment efficiency was in order of: Fenton > H_2O_2/O_3 > ozonation > catalytic ozonation with metal oxides. In ozonation, for effluents with higher COD, 60% COD reduction was observed after 1 h. Fenton process showed 88% and 50% COD reduction for secondary and raw wastewater. Optimum chemicals concentration ratios were 0.5 mol/1 mol Fe^{+2}/H_2O_2 and 2 mol/1 mol H_2O_2/COD.

Assalin et al. (2009) investigated the treatment of paper mill effluent for COD, TOC, total phenols and color removal using combined activated sludge-ozonation

processes and as well as independent processes. The combined activated sludge-O_3/pH 10 treatment was able to remove around 80% of COD, TOC and colour from Kraft E_1 effluent. For the total phenols, the efficiency removal was around 70%. The ozonation post treatment carried out at pH 8.3 also showed better results than these processes independently. The COD, TOC, colour and total phenols removal efficiency obtained were 75.5, 59.1, 77 and 52.3%, respectively. Gonzalez et al. (2010) studied the degradation of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) via biological, advanced oxidative process (AOP) and sequential biological-AOP processes. The white-rot fungus *Trametes pubescens* was used for the biodegradation of chlorophenols, while in AOP TiO_2/UV was used. In the biological degradation, the effect of glucose as a cofactor was also evaluated. The highest degradations were obtained when the reaction medium was supplemented with glucose, ranging from 94.6% to 37.8%, with degradation activity for 2-CP > 2,4-DCP > PCP > 2,4,6-TCP and the obtained degradation range from 82.0% to 24.0%.When biological removal process, supplemented with glucose, was followed for an AOP process, 100% degradation was obtained for all the chlorophenols tested.

2.8 LACUNAE

Although the heterogeneous and homogeneous photocatalytic processes has been widely recognized for wastewater treatment, limited studies has been reported on its application at industrial scale, with specific reference to treatment of organic compounds present in bleach mill effluents of agro residue based pulp and paper mill. Only few scattered reports are available on the use of mixed semiconductors or alternative catalyst to TiO_2. Moreover, study on the use of mixed catalyst on presence of artificial and solar light is not well documented. As on date, the observations

reported by other researchers indicate that the anaerobic and other biological methods have limitation of extended retention time required for treatment in addition to incomplete mineralization.

Depending on the type of wastewater, the nature of compounds and their concentrations, the the treatment processes necessitate integration of photocatalysis and biological processes which still remains to be explored. Non-biodegradable effluents are necessary to be pre-treated by advanced oxidation processes so as to reduce the toxicity and enhance the biodegradability of the wastewater.

The present study therefore attempted to demonstrate the application of AOP treatment of some model compounds dominantly present in pulp and paper mill effluents and examines the potential of AOP integrated treatment schemes for enhancing the degradation of pulp and paper mill effluents.

3.0 MATERIALS & METHODS

3.1 MATERIALS

3.1.1 Chemicals

Titanium dioxide, $Zn(NO_3)_2.6H_2O$, ethanol, acetonitrile (HPLC grade), methanol (HPLC grade), ortho-phosphoric acid, diethylene glycol, diethyl ether, acetone, phosphate buffer, n-hexane, acetic anhydride and sodium bicarbonate were procured from Ranbaxy Laboratories, India. 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG) were procured from Aldrich, USA and used as such without further purification. Sodium hypochlorite (4% available Cl_2), HCI and NaOH were obtained from Merck. Potassium dichromate, sulfuric acid, ferrous ammonium sulfate, silver sulfate, mercuric sulfate, ferroin indicator, potassium permanganate, sodium thiosulfate, potassium iodide and starch indicator were purchased from S.D. Fine chemicals, India. Reagents used for TOC was provided by Hach, USA. Double distilled MilliQ water (Millipore Distillation unit) was used for preparation of solutions.

3.1.2 Photocatalyst

Titania P-25 (surface area 50 m^2/g and average particle size 30 nm) was obtained from Degussa, Germany and was used as received. ZnO (5 m^2/g) was purchased from Merck, Germany and were used as such.

3.1.3 Effluent samples

The first set of composite effluent samples were collected from the chlorination (C) and first alkaline extraction (E_1) stages of soda pulp bleaching section of an agro residue (wheat straw) based pulp and paper mill in Punjab province of India. Second set of composite effluent samples were procured from functional effluent treatment plant (ETP) of pulp and paper mill which consisted of sequential

up-flow anaerobic sludge blanket digester (UASB) followed by two stage (Aerobic-I and Aerobic-II) activated sludge process (ASP) . The samples were collected from three different stages of ETP *viz.* inlet to ETP after primary clarification (*raw*); after anaerobic treatment (*Stage-1)* and after anaerobic and single stage aerobic-I (*Stage-2*) treatment as shown in Fig. 3.1. For collection of samples, the vessels were cleaned and rinsed carefully with distilled water and then washed with sample before sample collection. The samples were transported and stored at 4^{o}C.

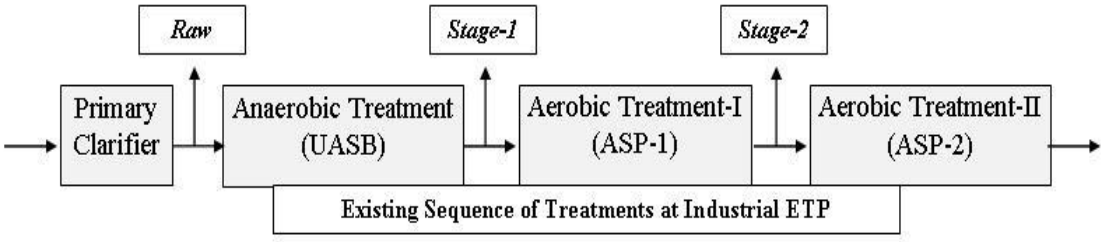


Fig. 3.1: Flow diagram showing sampling points (in italics) from functional pulp and paper mill effluent treatment plant

3.1.4 Inoculum preparation

The biomass activated sludge was collected from the underflow of secondary settling Tank (SST) of functional ETP of the mill. The biomass was pelleted and transferred to a fresh medium containing Luria Broth (LB).

3.2 EQUIPMENTS AND INSTRUMENTS

3.2.1 Photocatalytic reactor

The UV reactor (rectangular) was made up of cast iron sheets with wooden roof equipped with seven UV tubes of 36W (Philips) each having wavelength of 365 nm as shown in Figure 3.2. Maximum UV intensity was found to be 25 W/m^2 at the middle of the UV reactor and all experiments were performed at this UV intensity. The photon flux was approximately 0.625 W. For solar insolation experiments, the borosilicate glass reactors of diameter 0.18 m and 1000 ml capacity, facilitated with

ports at the top for sampling, gas purge and gas outlet, were used. The solar experiments were performed in day time between 10.00 h to 16.00 h in the month of April-May. The average intensity of sunlight in this region was 35 W/m^2 during the experiments.

3.2.2 Radiometer

The intensity of ultraviolet light was measured in the UV reactor with the help of radiometer (EPPLEY, USA).

3.2.3 pH meter

Thermo Orion 920A pH meter was used to measure the pH of the solution. The pH of solution was adjusted by adding 1.0 M HCl or NaOH solution as per requirement.

3.2.4 Syringe filter

Millipore syringe filter of 0.45 μm was used to filter the samples.

3.2.5 Thermoreactor and COD meter

Hach thermoreactor and Hach DR 820 colorometric COD meter was used for analysis.

3.2.6 Spectrophotometer

The spectra were taken with UV-vis spectrophotometer (Hitachi V-500UV/Vis) Japan. Perkin Elmer Lamda 750 UV\Vis\NIR spectro-photometer was used for recording UV-Vis transmittance spectra in air at room temperature in the wavelength range of 200–700 nm.

2.7 X-ray powder diffractometer

Rigaku D/max-III C diffractometer was used for X-ray powder diffraction (XRD) analysis of the photocatalyst at room temperature using Cu-Kα radiation (λ = 0.15418 nm), over the 2θ collection range of 20–100°.

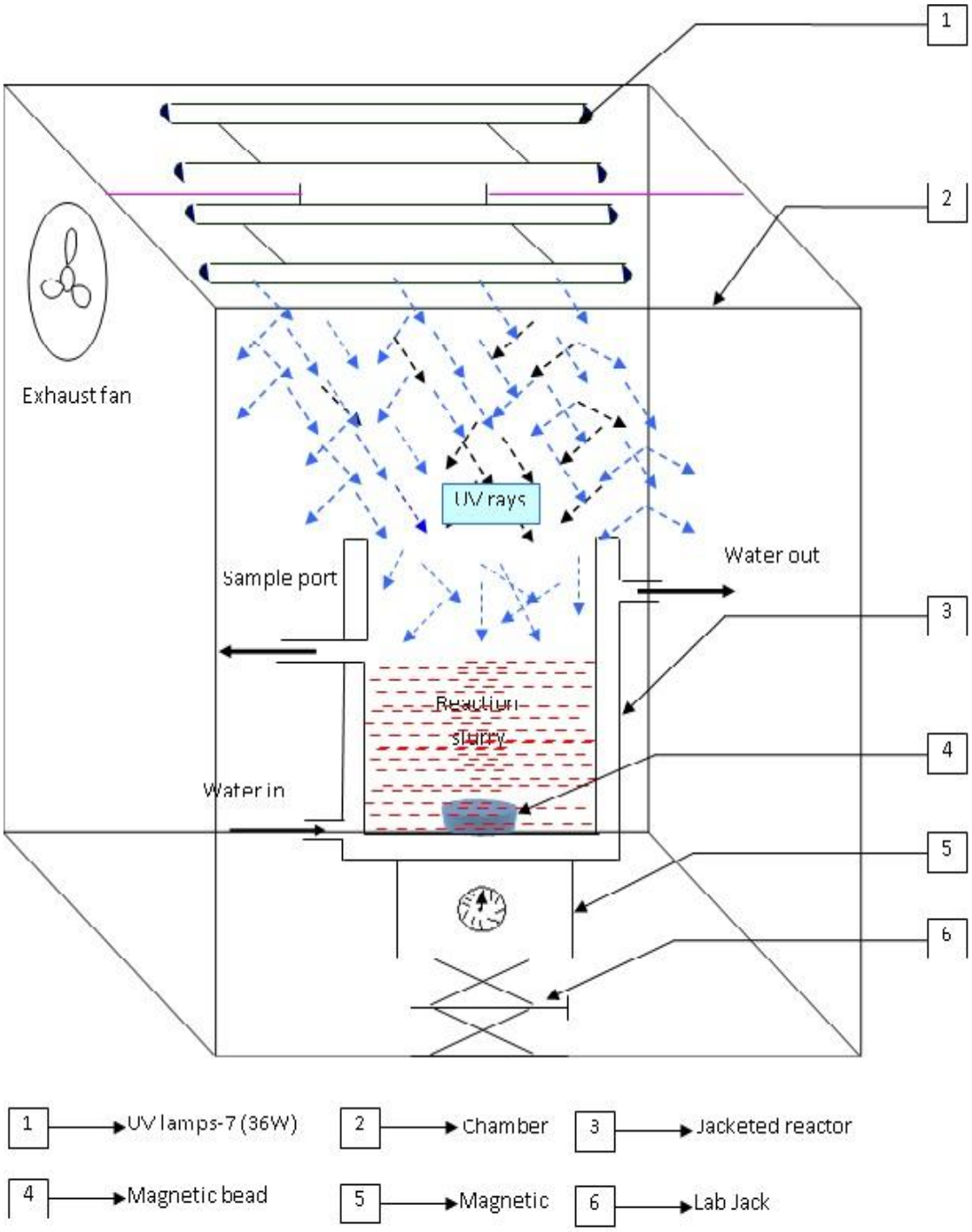


Figure 3.2: Experimental Setup for Photocatalysis

3.2.8 Scanning electron microscope

Scanning electron microscope (SEM, Hitachi-S-3400N) was used to obtain microscopic feature of catalyst using fine catalyst powder supported on carbon tape and coated with gold.

3.2.9 High performance liquid chromatography (HPLC)

HPLC (Agilent Technologies 1120 Compact LC) consisting dual-solvent delivery system, a 490 programmable multiwavelength UV absorbance detector, an automated gradient controller, and a 30 cm Bondapack C18 column (Agilent HPLC columns having dimension of 250×4.6 mm) was used to determine concentration of model compound(s) in phototreated samples.

3.2.10 Gas chromatography/mass spectrophotometer

Model compounds in the wastewater were evaluated qualitatively and quantitatively using GC-MS (Polaris Q Thermo Electron Corporation) technique. The conditions for analysis in GC-MS are given in Table 3.1.

Table 3.1: GC and MS conditions for the analysis of chlorophenolics

GC		**MS**	
Parameters	**Conditions**	**Parameters**	**Conditions**
Detector	Mass spectrometer	Ionisation mode	Electron
Carrier gas (flow rate)	Helium (1mL/min)	Ionising energy (eV)	70
Sample injected (µL)	1		
Injection mode	Split less		
Column dimensions	30 m x 0.25 mm		
Film thickness	0.25 µm		
Injector temperature	210		
Column temperature (^{0}C)	45 for 1 min		
	45-280 at 6 ^{0}C/min		
	280 for 25 min		

3.3 METHODS

3.3.1 Determination of chemical oxygen demand (COD)

COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The degradation efficiency of effluents was expressed with reference to the decrease in COD (Chemical oxygen demand) measured by closed reflux method (spectrophotometric) using standard protocols [APHA, 1998]. Test solution (2 ml) was pipetted into the standard amount of potassium dichromate oxidizing mixture and digested at 150^{o}C for two hours. The intensity of the resultant coloured solution was measured colorometrically against blank sample.

3.3.2 Determination of biochemical oxygen demand (BOD_5)

BOD is the oxygen required for the biochemical degradation of organic material. This analysis was done by BOD Trak system (HACH). The dilutions were prepared according to the standard protocol [APHA, 1998].

3.3.3 Determination of solids

Total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) were determined by using standard methods (2540 B, C and D) [APHA, 1998].

3.3.4 Determination of chloride content

Chloride ion concentration was measured using standard method 4500 Cl^- B Argenometric method [APHA, 1998].

3.3.5 Biodegradability assay

The Zahn–Wellens test was carried out according to the EC protocol (Directive 88/302/EEC) to assess the biodegradability potential of the C and E_1 effluents using the activated sludge obtained as inoculum. The inoculum was centrifuged at 10,000 rpm (8496 g) for 7 min at 20^{o}C in Hitachi (RX-11 Series) and washed once with mineral medium. The ratio between the carbon content of the

experimental sample and the dry-weight of the inoculum was maintained between 1 and 4 (average 3.2). Optimum aeration and mixing was provided during the experiment.

3.3.6 Determination of total organic carbon (TOC)

The degradation of BME was also expressed with reference to the decrease in total organic carbon (TOC) measured by Hach DR 890 Colorimeter (Method # 10129: Hach, USA).

3.3.7 High performance liquid chromatography (HPLC) technique

The degradation of 4-CC and 4-CG was assessed using a high-performance liquid chromatograph (Agilent Technologies 1120 Compact LC). The mobile phase used was 70:30 %v/v HPLC grade acetonitrile : aqueous phosphoric acid (pH 3). In case of 4-CG the mobile phase was 70:30 %v/v HPLC grade methanol: water. UV detection was performed at 283.0 and 281.5 nm for 4-CC and 4-CG, respectively. The unit was operated isocratically at the rate of 1.0 ml/min.

3.3.8 Gas chromatography – mass spectrometric (GC-MS) technique

Qualitative and quantitative analysis of the model compounds in the wastewater was evaluated using GC-MS technique. The extraction of chlorophenolic compounds has been carried out according to the procedure suggested by Lindstrom and Nordin (1976) using diethyl ether: acetone (90:10) solution. The chlorophenols are converted to readily volatile acetyl derivatives prior to GC-MS analysis. The acetylation was done with acetic anhydride based on procedure given by Abrahamsson and Xie (1983). For extraction, the pH of 1000ml of effluent was adjusted to 2.0 with concentrated H_2SO_4 and 400 mL of 90:10 diethyl ether/acetone mixture was added to it. The resulting solution was shaken intermittently for 48 h. The whole etheral extract was transferred to 500 mL separating funnel. In order to remove acidic impurities, 5 mL of 0.5 M $NaHCO_3$ was added to the solution.

Thereafter, the ether layer was shaken with 5 mL of 0.5 M NaOH to extract chlorophenolics. Aqueous NaOH layer was separated and washed with 10 mL of fresh diethyl ether.

Before injecting into GC column, the extracted chlorophenolics were acetylated. In each case 4.5 mL of wastewater extract (4 mL diluted to 4.5 mL with distilled water) was taken in a PTFE lined screw capped glass tube. 0.5 mL of 0.5M Na_2HPO_4 buffer solution was added to the glass tube and shaken for 2 min. Then 0.5 mL of acetic anhydride was added for derivatization of chlorophenolics and 1mL of n-hexane was added for the extraction of the acetyl derivatives of chlorophenolics. The mixture was shaken for 2 min and 1µL of acetyl derivative from the hexane layer was injected into the GC column.

3.4 PREPARATION OF NANOSIZED HETEROSTRUCTURED ZnO/TiO_2 PHOTOCATALYSTS

TiO_2 and Zn $(NO_3)_2.6H_2O$ were used as starting materials, and NaOH was used as the precipitant without further purification. $Zn(NO_3)_2.6H_2O$ was dissolved in a minimum amount of deionized water with constant stirring until clear solution was obtained and 1M NaOH solution was added, white amorphous precipitates of $Zn(OH)_2$ were formed. The required amount of TiO_2 was added with constant stirring for the preparation of the heterostructured ZnO/TiO_2 photocatalysts with the Zn/Ti molar ratios of 9:1 by maintaining pH 7. The precipitates were stirred for 20 h for homogeneous mixing. The precipitates were filtered and washed with deionized water to remove the soluble ions. The wet powder obtained was dried at 100°C in air to form the precursors of the heterostructured ZnO/TiO_2 photocatalysts which were further calcined at 250°C in air for 3 h. The nanosized photocatalyst obtained in powder form was labeled as Z_9T (Zn/Ti molar ratios of 9:1)

3.5 CHARACTERIZATION OF NANOPHOTOCATALYST

3.5.1 Band-gap

The important parameter of a semiconductor is its band-gap (Eg) i.e. the energy difference between the top of its valence band and the bottom of its conduction band. Optical absorption provides the information of the band-gap (Eg). In the optical absorption measurements, light of different wavelengths are directed at normal incidence on the sample. The ratio of the incident and transmitted intensity are strongly dependent on the energy of the photon and the sample thickness. The photons with energies (hυ) less than the band-gap will be transmitted while the photons with energy higher than the band-gap are absorbed. The intensity of the light absorbed/transmitted by the material in the absorption spectra is strongly dependent on the material thickness and expressed by following for particular wavelength

$$I = I_o \times e^{-\alpha d}$$

$$\alpha = 1/d\ [\ln(T)]$$

Where α is absorption coefficient, d thickness of film (1500 nm) and T is transmittance. The output of the spectrophotometer was in the form of transmittance w.r.t. I. was calculated using above equation. hυ was calculated at different wavelengths. The energy band gap of sample has been calculated according to the above equation widely adopted for crystalline semiconductors [Fu et al., 2006; Maruyama et al., 2006].

$$\alpha h_\upsilon = A\ (h_\upsilon - E_g)^{(n/2)}$$

Where α, υ, A, Eg and n are the absorption coefficient, incident light frequency, constant, band gap, and an integer (normally equal to 1, 2, 4, or 6), respectively. The α and υ values at the steep edges of the transmission spectra were used to construct the plots of $(\alpha\ h\upsilon)^{1/2}$ against photon energy. The band gap of the

sample was determined by the intersection of the extrapolated linear portion of the plot with the energy axis.

3.5.2 Structure and morphology of photocatalyst

To study structure and morphology of the photocatalysts, the SEM unit was operated at 15 kV of accelerating voltage and SEM photograph was taken.

3.5.3 Crystallite size

The average crystallite size of photocatalysts was calculated using the following Scherrer Equation [Tian et al., 2009].

$$t = K\lambda / B \cos\theta$$

Where K is a coefficient = 0.9, λ = 0.1541 nm, B (in radian, r=θ/57.27) is the full width half maximum (FWHM) of the catalyst and θ is the diffraction angle.

3.5.4 Crystallanity

The nature of the nanophotocatalyst in terms of its crystallanity and determination of lattice points was determined using XRD. The accelerating voltage of 40 kV, emission current of 30 mA and the scanning speed of 4.4 counts per second were used.

3.6 EFFLUENT ANALYSIS

The industrial effluent samples were collected as discussed in section 3.1.3 and analyzed for different characteristics such as COD, BOD, TOC, TSS, TDS, pH, chlorides, etc. following standard protocols mentioned in section 3.3.

3.7 MODES OF EXPERIMENTS

3.7.1 Slurry mode experiments

The photocatalytic experiments were performed in specially designed double walled reaction vessels (1000 ml) having surface area of 0.025 m^2**.** For the slurry

mode experiments, photocatalyst in the form of powder was added to a solution to be degraded. The solutions were kept under constant stirring using magnetic stirrers and aeration was carried out with the help of conventional aerators. The ambient temperature of the reaction vessel and UV chamber was maintained at 30±0.5 ^{o}C by circulating the water in double walled reaction vessels and providing air exhaust. The aqueous suspension was aerated and magnetically stirred at moderate rpm so that the catalyst remains in the form of suspension.

3.7.2 Immobilized mode experiments

In the immobilized mode, the photocatalysts ZnO, was fixed on to an inert support (pumice stone thoroughly washed with excess water) by using the procedure given by Noorjahan et al. (2003). The reactor of diameter = 0.2 m, and capacity 1000 ml was used. In brief, immobilized ZnO was suspended in minimum amount of water (4 g of ZnO in 100 ml of water) and 5ml of acrylic emulsion was added to it under stirring in a span of 30 minutes. The mixture of ZnO and acrylic emulsion was spread on pumice stone with a laboratory spray gun. The coated ZnO film was air dried and coating was repeated thrice to get a uniform film without pin holes. The degradation experiments were carried out under solar illumination.

3.8 ADSORPTION EXPERIMENTS

The adsorption tests under dark conditions were carried out in order to evaluate the adsorption of model compounds (4-CC and 4-CG) on the photocatalyst surface. These tests were performed using 100 ml aqueous solution of model compound in contact with optimum amount of photocatalyst and kept in dark at 25^{o}C. The solution was filtered through 0.45 μm filter and concentration of the unadsorbed substrate was measured to find the extent of adsorption.

3.9 DEGRADATION STUDIES

3.9.1 Model compounds

For the degradation of model compounds (2-MP, 4-CC, 4-CG), photocatalytic experiments were conducted by adding fixed amount of photocatalyst (TiO_2 / ZnO, their mixture etc.) taken with or without oxidant (NaOCl) in slurry mode to 100 ml sample solution of known concentration (25 mg/L 2-MP, 50 mg/L 4-CC, 25 mg/L 4-CG,). The aqueous suspension was subjected to irradiation under UV/solar light. At different time intervals, aliquot was taken out with the help of syringe and then filtered through Millipore syringe filter of 0.45 μm. Then absorption spectra of sample solution were recorded at λ_{max} (275 nm for 2-MP, 283 nm for 4-CC and 281.5 nm for 4-CG). The degradation of the models compounds was assessed by monitoring absorbance as a function of irradiation time using spectrophotometer in the wavelength associated with the concerned compound. The degradation efficiency was calculated as follows:

$$Degradation Efficiency(\%) = 100 \times \left[\frac{C_o - C}{C_o} \right]$$

where C_0 is initial concentration of solution and C is concentration of solution after photoirradiation. The experimental matrix was developed by varying the dose of photocatalysts, pH of the solution, concentration of oxidant and initial concentration of substrate. COD reduction was evaluated for 2-MP in order to track its degradation. The products of degradation of 4-CC and 4-CG were further analyzed using HPLC.

3.9.2 Bleach mill effluents (BME)

C and E_1 stage bleach mill effluents were subjected to independent photocatalytic, biological as well as sequential Photocatalytic-biological (Photo+Bio) and biological-photocatalytic (Bio+Photo) treatments. Photocatalytic experiments were carried out at normal pressure under slurry mode in specially designed double

walled glass reaction vessels placed in UV reactor. In order to optimize the photocatalytic process parameters, the experimental matrix was developed in which the dose of photocatalyst (1.0 – 3.0 g/L), initial pH of the test effluents (2-12) and NaOCl concentration (0.005-0.015 M) was varied and subjected to irradiation under UV/solar light upto 6 h. Aeration was facilitated through the aqueous suspension with the help of aquarium aerators. At 2 h time intervals, aliquots were collected using syringe filter and COD was recorded in order to assess the degradation efficiency. All the tests were carried out in triplicate for reproducibility of results.

For Biological experiments, 100mL of effluent was taken in 250 mL Erlenmeyer flasks and 40 mL of acclimatized sludge, with approximate ratio of 4:1:: Carbon : sludge, was added to it. The initial pH was adjusted to 7.0. The flasks were incubated at 30±1 ^{o}C and 120 rpm for 21 days to study the degradation of organics by the inoculum. A parallel control experiment was performed with incubation of inoculum and diethylene glycol (0.5 g/L) as carbon source, simultaneously to test the sludge activity. Samples (10 ml each) were drawn after 24 h and centrifugated at 10,000 rpm (g = 8496) for 5 min. at 20^{o}C. The filtrate samples were analyzed for their COD values.

Photocatalytic – biological (Photo+Bio) treatment and the reverse sequence (Bio+Photo) were applied in order to evaluate the efficiency of the sequential treatment on selected effluent samples. The photocatalytic reactions were carried out under optimized conditions. In Photo+Bio integrated approach, effluent samples were degraded in the photocatalytic experiment using UV/TiO_2 or solar/ZnO for a short span and then the phototreated effluents were subjected to biological treatment upto 24 h. In the second integrated approach (Bio+Photo), the effluents were biologically treated for 24 h and then these biotreated effluents were degraded using UV/TiO_2 or solar/ZnO photocatalytic systems. The degradation efficiency was recorded in terms

of COD reduction. The extent of degradation in sequentially treatment effluent samples was also expressed with reference to the decrease in TOC values.

3.9.3 Combined pulp and paper mill effluents

Composite *raw* (primary clarified), *stage-1* (after anaerobic treatment) and *stage-2* (after anaerobic followed by aerobic-I treatment) effluent samples collected from functional ETP of agro-residue based pulp and paper mill were subjected to photocatalysis under slurry mode. In order to optimize the photocatalyst dose, experiments were conducted by varying TiO_2 and ZnO dose from 1.0 to 3.0 g/L, under UV irradiation for 6 h. At an interval of 2 h, aliquots were collected using syringe filter and COD was measured to assess degradation of the effluents. All the tests were carried out in triplicate.

In order to carry out aerobic treatment after photocatalysis, 100mL of photo-treated sample was taken in 250 mL Erlenmeyer flasks and the initial pH was adjusted to 7.0. 40 mL of inoculum was added to the flasks and incubated at 30±1 ^{o}C and 120 rpm for 21 days. A control was maintained by incubating inoculum with diethylene glycol (0.5 g/L) as carbon source, to examine the microbial activity. Samples (10 ml each) were drawn after 24 h and centrifuged at 8500g (Hitachi RX-11) for 5 min. at 20^{o}C. The filtrate samples were analyzed for their COD values.

The sequential photocatalytic followed by aerobic treatment was employed to both *stage-1* and *stage-2* effluent samples to affect integrated anaerobic-photocatalytic-aerobic and anaerobic-aerobic-photocatalytic-aerobic sequence, respectively (Fig. 3.3). The photocatalytic reactions were carried out under optimized conditions using TiO_2 or ZnO in the presence of solar irradiation. The photo-treated samples were further subjected to biologically treatment for 24 h, as defined earlier.

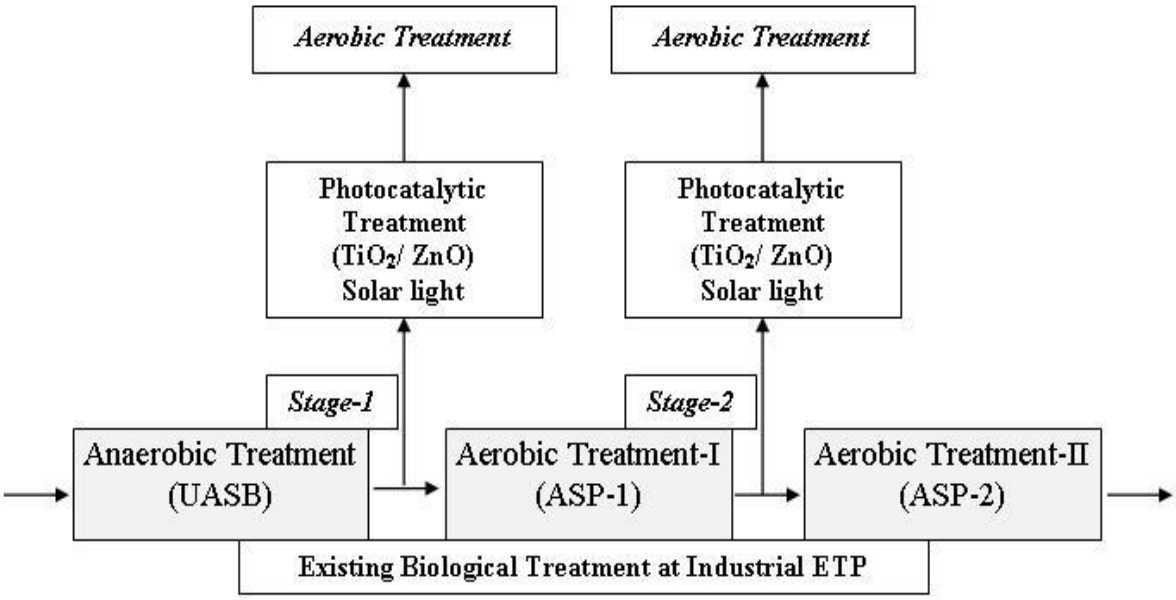


Fig. 3.3: Coupled treatment scheme for combined pulp and paper mill effluents

In order to increase the industrial viability of the integrated treatment, the degradation of *stage-2* effluent was also investigated by immobilizing ZnO as mentioned in section 3.7.2 under solar irradiations. 100 ml of *stage-2* effluent was taken and treated with immobilized ZnO under solar irradiation. The degradation efficiency was recorded in terms of COD reduction.

4.0 RESULTS

This chapter deals with the degradation of substituent phenolic compounds, bleach and combined mill effluents of an agro residue (wheat straw) based pulp and paper mill. Bleach mill effluents (BME) are the chlorination (C Stage) and first alkaline extraction stage (E_1 Stage) effluents of soda pulp mill and studies with reference to their degradation was carried out with independent biological, photocatalytic as well as sequential biological-photocatalytic (Bio+Photo) and photocatalytic-biological (Photo+Bio) processes. Degradation of organics was assessed in terms of COD and TOC/ chromatographic studies (GC-MS). The combined pulp and paper mill effluent samples were collected from the functional effluent treatment plant (ETP) at inlet point after primary clarification (*Raw*); after anaerobic (UASB) treatment (*Stage-1*) and after sequential anaerobic-aerobic-I (UASB-ASP) treatment (*Stage-2*). The *stage-1* and *stage-2* effluents were subjected to independent photocatalytic and integrated photocatalytic-biological processes in order to employ sequential treatment sequences namely anaerobic-photocatalytic-aerobic and anaerobic-aerobic-photocatalytic-aerobic, respectively. The efficiency of treatment was evaluated in terms of COD reduction. In order to make the process economical, the efficiency of solar light was evaluated in the heterogeneous photocatalysis. The efficacy of the photocatalyst was also adjudged in immobilized and slurry modes.

4.1 Physicochemical characteristics of the effluents

The effluent samples from different sections of functional ETP of pulp and paper mill were analyzed for different characteristics such as COD, BOD, TOC, TSS, TDS, pH, etc. following standard methods. Table 4.1 presents the physicochemical

characteristics of the *raw, stage-1 and satge-2* effluent samples. The high chemical oxygen demand (COD) and total dissolved solids (TDS) of the effluents indicated the presence of significant levels of organic and inorganic constituents. Table 4.2 presents the physicochemical characteristics of C stage and E_1 stage bleach mill effluents. The Zahn-Wellens test was performed in order to assess the biodegradability of C and E_1 effluents in terms of COD removal. The results showed less biodegradability of C effluent (26%) as compared to E_1 effluent (48%) in the tested conditions. This test conditions were similar to those of an industrial effluent treatment plant using activated sludge. The residual COD in C effluent showed that its level did not change appreciably during a long period of retention time (21 days). This indicated that acclimatized bacteria could not adapt to and degrade C effluent. However, in case of E_1 effluent, the moderate biodegradability was observed since reduction in COD was 48%. A parallel control experiment carried out using diethylene glycol (0.5 g/L) showed 94% degradation in 5 days which indicated that the sludge was otherwise active. The extent of biodegradation of E_1 over C effluent was also evident through BOD_5/COD ratio which was 0.62 and 0.34 respectively.

The C stage bleach mill effluent was subjected to gas chromatographic analysis in order to identify the organic compounds present in the effluent. The existence of substituent phenolic compounds was further established and quantified using GC-MS protocols (Fig. 4.1). The compounds present in C stage bleach mill effluent along with their retention times are shown in Table 4.3. Out of various compounds identified, 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG) were selected for further studies.

Table: 4.1. Characteristics of effluent samples from pulp and paper mill ETP

S.N.	Parameter	*Raw* effluent	*Stage-1* effluent	*Stage-2* effluent
1	pH (n=11)	7.3 (± 0.01)	6.7 (± 0.01)	8.2 (± 0.01)
2.	TSS (mg/L) (n=6)	700.0 (± 30.0)	430.0 (± 21.0)	160.0 (± 9.0)
3.	TDS (mg/L) (n=8)	3690.0 (± 40.0)	2836.0 (± 32.0)	2100.0 (± 23.0)
4.	BOD_5 (mg/L) (n=5)	1780.0 (± 33.0)	680.0 (± 18.0)	56.0 (± 3.0)
5.	COD (mg/L) (n=19)	3780.0 (± 48.0)	1776.0 (± 36.0)	600.0 (± 20.0)
6.	TOC (mg/L) (n=16)	1130 (± 42)	580 (± 24)	240 (± 16)

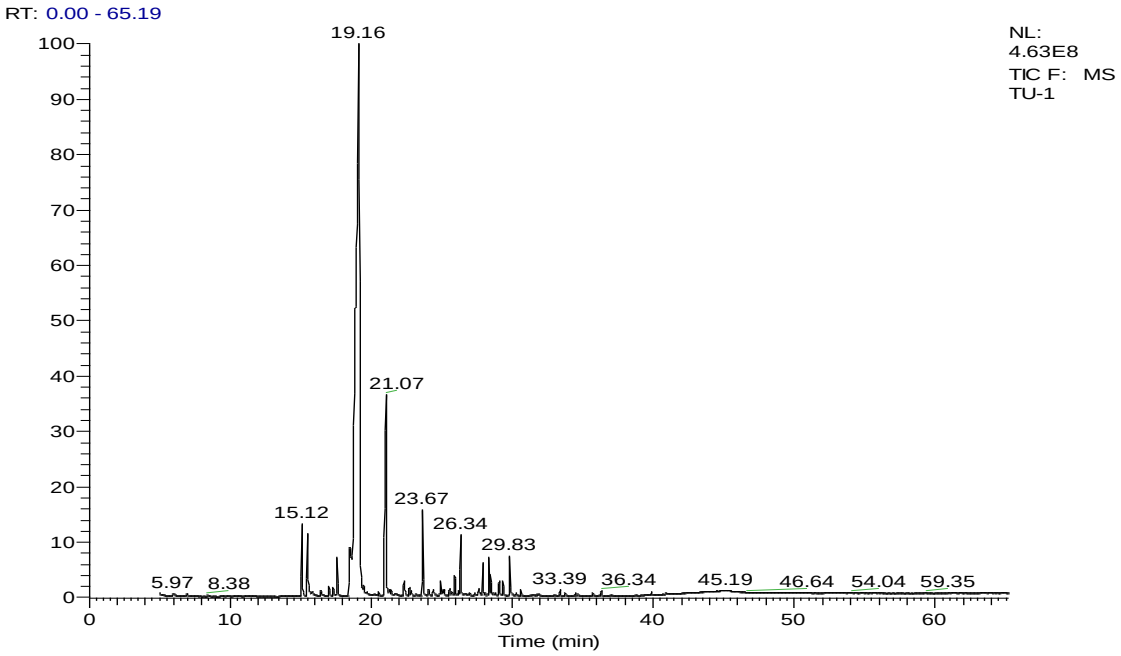


Fig. 4.1: GC-MS chromatogram of raw bleach mill effluent (C stage)

Table: 4.2. Characteristics of C stage and E_1 stage bleach mill effluent samples

S.N.	Parameter	C Stage effluent	E_1 Stage effluent
1.	pH (n=11)	1.9 (± 0.01)	8.2 (± 0.01)
2.	TDS (mg/L) (n=8)	4030.0 (± 32.0)	2500.0 (± 23.0)
3.	SS (mg/L) (n=8)	150.0 (± 10.0)	200.0 (± 14.0)
4.	BOD_5 (mg/L) (n=5)	675.0 (± 5.0)	1386 (± 11.0)
5.	COD (mg/L) (n=19)	2010.0 (± 18.0)	2240.0 (± 21.0)
6.	TOC (mg/L) (n=16)	400.0 (± 20.0)	560.0 (± 24.0)
7.	Chlorides (mg/L) (n=8)	2626.3 (± 20.7)	1753.4 (± 16.6)

The photocatalytic degradation of model compounds such as 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG) typically found in bleach mill effluents was performed in slurry mode under UV/solar irradiations. The photocatalytic activity of catalysts like TiO_2 / ZnO was assessed for degradation of 4-CC and 4-CG. The effect of various process parameters like catalyst dose, pH, oxidant concentration and light source (UV/solar) has been examined. The degradation efficiency was evaluated in terms of changing absorbance, reduction in chemical oxygen demand (COD)/ high performance liquid chromatography (HPLC). An attempt was also made to explore the possibility of utilizing mixed photocatalyst system comprising of ZnO and TiO_2 for the degradation of 4-CG. Nanophotocatalyst comprising 90% ZnO and 10% TiO_2 was synthesized, characterized and its photocatalytic activity was evaluated for degradation of 4-CG.

Table: 4.3. Identification of chlorinated phenolics in C stage bleach mill effluent

S.N.	Retention Time	Compound Identified
1	RT-15.12	2-methoxy phenol
2	RT-15.51	2methoxy-4chlorophenol
3	RT- 18.70	4-chloroguaiacol
4	RT-19.16	2-methoxy-6-chlorophenol
5	RT-21.07	1,2-diacetoxy-3-chlorobenzene
6	RT- 23.67	4-chlororcatechol
7	RT-26.34	Dichloro naphtalenol
8	RT-29.83	2-acetoxy methyl-3-acetoxy-4(H) pyran-4-one

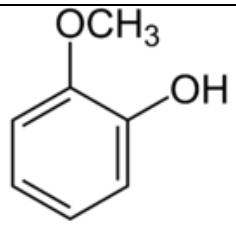
The study is presented through following sections:

- Photocatalytic degradation of 2-methoxy phenol (2-MP)
- Photocatalytic degradation of 4-chlorocatechol (4-CC)
- Photocatalytic degradation of 4-chloroguaiacol (4-CG)
- Photocatalysis using mixed/ hetero-structured nanophotocatalyst system
- Coupled biological and photocatalytic treatment of bleach mill effluents
- Integrated photocatalytic and biological treatment of combined pulp and paper mill effluents

4.2 PHOTOCATALYTIC DEGRADATION OF 2-METHOXY PHENOL

2-methoxy phenol (2-MP) or commonly termed as guaiacol is a substituent phenolic group usually found in bleach mill effluents. Guaiacol is a precursor to various flavorants such as eugenol and vanillin. Its derivatives are used medicinally as an expectorant, antiseptic, and local anesthetic. 2-MP was purchased from Sigma Aldrich, USA and used as such. In 2-MP, -OCH_3 group is non polar so it is less soluble in water, but soluble in ethanol due to the presence of –OH group. The chemical structure and physical properties of 2-MP are given in Table 4.4.

Table: 4.4. Characteristics of 2-methoxy phenol (2-MP)

Name of the model compound	**Guaiacol**
Synonym	o-Methoxyphenol; Methylcatechol
IUPAC	2-methoxy phenol
CAS No.	90051
Molecular Formulae	$C_7H_8O_2$
Molecular weight	124.14 g/mol
Density	1.112 g/cm^3, liquid
Melting Point	28 ^oC
Boiling point	204-206 ^oC
Flash Point	28 ^oC
Λmax	275 nm
Structure	

The photocatalytic degradation study of 2-methoxy phenol was carried out using TiO_2 in the presence of UV/solar irradiation. The effect of process parameters viz. catalyst dose, pH and oxidant concentration (NaOCl) were assessed for the degradation of 2-MP.

4.2.1 Time dependent degradation of 2-MP

Fig. 4.2 shows the typical time dependent UV-Vis spectra of photocatalytic degradation of 2-MP (25 mg/L) in aqueous solution with TiO_2 (2 g/L). The absorption peak was observed at 275 nm which decreased gradually during photocatalysis, thus indicating the degradation of 2-MP.

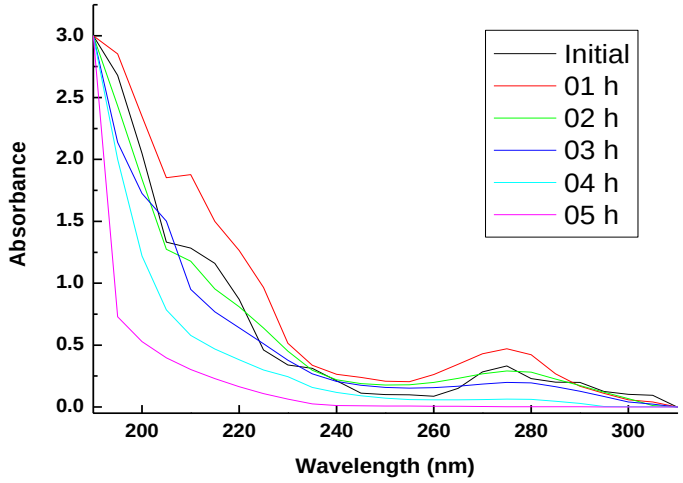


Fig. 4.2: Time dependent photocatalytic degradation of 2-MP (2-MP: 25 mg/L; TiO_2 dose: 2 g/L; Irradiation time: 5 h)

4.2.2 Effect of photocatalyst loading

The amount of catalyst plays an important role in the degradation of the organic compound in photocatalysis. It is necessary to find the optimum loading for the efficient removal of the organic compound in order to avoid the use of excess catalyst. The effect was studied by varying TiO_2 from 0.5 to 3.0 g/L for the degradation of 2-MP (25 mg/L) at pH (6.7) for 5 h of UV exposure (Figure 4.3). The degradation was studied in terms of decrease in absorbance at λ_{max}. The results reveal that minimum degradation of 14.3 % was observed with TiO_2 dose of 0.5 g/L. With the increase in catalyst dose to 2.0 g/L, the degradation efficiency enhanced to 86.7%, beyond which the efficiency declined to 73% at dosage of 3.0 g/L.

4.2.3 Effect of pH

The pH of the aqueous medium under treatment significantly influenced the surface-charge properties of the photocatalysts and in turn governed the rate of photocatalytic reaction taking place on surface of semiconductor particle. The experiments were performed at pH ranging from 2–12 using optimum dose of TiO_2

(2.0 g/L). Fig. 4.4 shows that the maximum degradation efficiency of 88.7 % was achieved at pH 6.0.

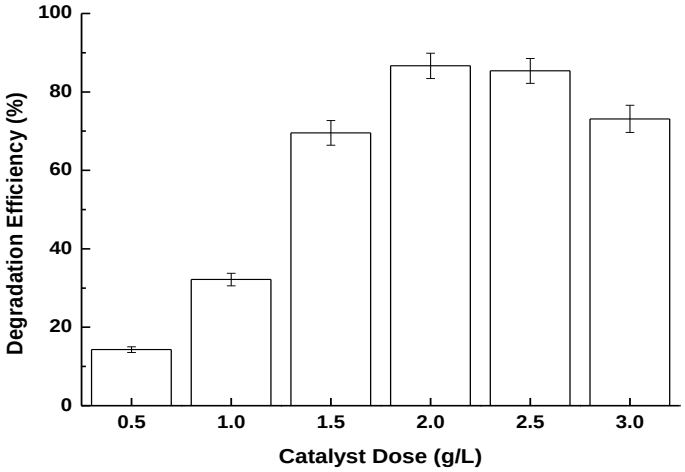


Fig. 4.3: Effect of TiO_2 dose on the degradation of 2-MP (2-MP: 25 mg/L; pH 6.7; Irradiation time: 5 h)

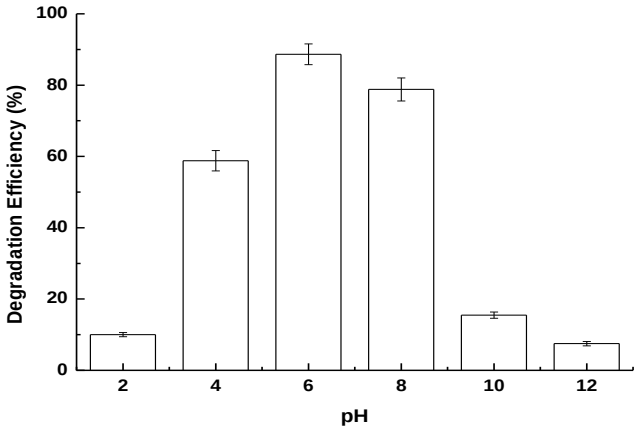


Fig. 4.4: Effect of pH on the degradation of 2-MP (2-MP: 25 mg/L; TiO_2 dose: 2.0 g/L; Irradiation time: 5 h)

4.2.4 Effect of oxidant concentration

Sodium hypochlorite was used as an oxidant in the concentration range of 0.02 to 0.06 M along with TiO_2 (2.0 g/L) at pH 6.0 and the effect of addition of oxidant was observed to be insignificant in the photocatalytic degradation of 2-MP.

4.2.5 Effect of the initial substrate concentration

The influence of initial concentration of the substrate on the photocatalytic degradation was assessed by varying the concentration of 2-MP in the range of 10–100 mg/L. As the initial substrate concentration of the solution increased from 10 to 100 mg/L, the degradation efficiency decreased consistently from 97.9 to 53.1% as shown in Fig. 4.5.

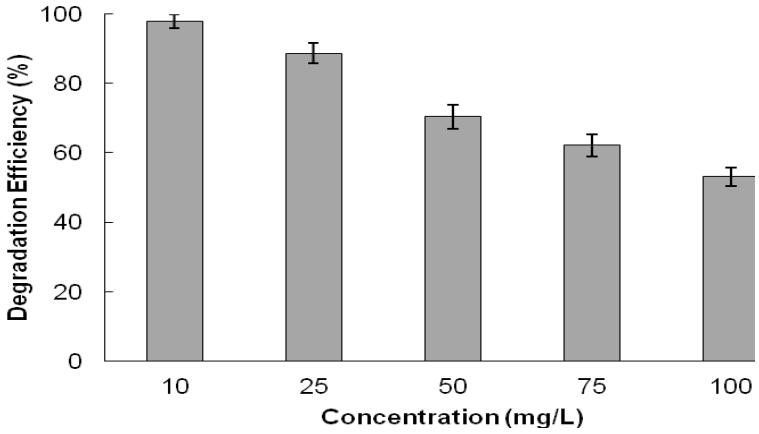


Fig. 4.5: Effect of initial concentration of 2-MP on the degradation efficiency (TiO_2 dose: 2 g/L; pH: 6.0; Irradiation time: 5 h)

4.2.6 Effect of the light source

The effect of light sources (UV/solar light**)** was assessed on the degradation of 2-MP (25 mg/L) under optimized conditions (TiO_2 2 g/L, pH 6) by exposing 2-MP aqueous solution to UV and solar light independently. Figure 4.6 shows the rate of photocatalytic degradation under optimized conditions which was found to be slightly more (91%) in the presence of solar light when compared to UV light (88.7%) after 5 h of irradiation exposure.

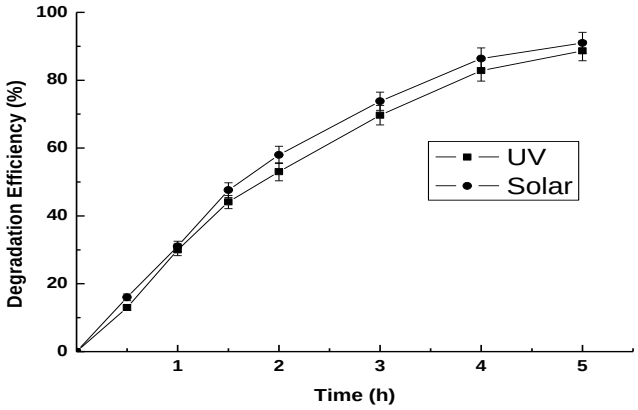


Fig. 4.6: Effect of light source on the degradation of 2-MP (2-MP: 25 mg/L; TiO_2 dose: 2 g/L; pH: 6.0; Irradiation time: 5 h)

4.2.7 Mineralization studies (pH dependent)

The mineralization of 2-MP was recorded in terms of COD reduction. Fig. 4.7 shows the reduction in COD at different pH values. The COD of the solution decreased from 144 to 10 mg/L under optimized conditions (TiO_2 dose 2g/L and pH 6.0) after 5 h of photocatalytic treatment with maximum degradation occurring at pH 6.0.

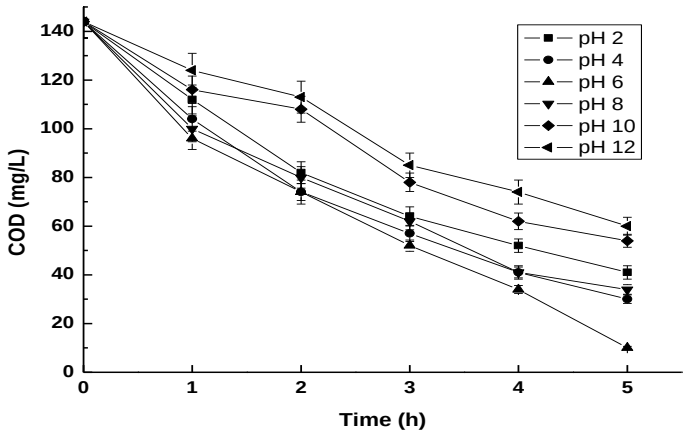
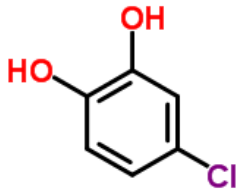


Fig. 4.7: COD reduction of 2-MP at different pH values (2-MP: 25 mg/L; TiO_2 dose: 2.0 g/L; Irradiation time: 5 h)

4.3 PHOTOCATALYTIC DEGRADATION OF 4-CHLOROCATECHOL

4-chlorocatechol (4-CC) having purity of 97% was procured from Aldrich, USA and used as such. 4-CC is versatile intermediate in chemical syntheses because both the hydroxyl group and the aromatic ring can react by both electrophilic and nucleophilic substitution. Electrophilic substitution is favoured by the presence of chlorine atoms on the aromatic nucleus. Nucleophilic substitution for one or more of the chlorine atoms is disfavoured by the presence of the other chlorine atoms. 4-CC is usually present in the effluents from bleach section of pulp and paper mill. The chemical structure and physical properties are given in Table 4.5.

Table: 4.5. Characteristics of 4-chlorocatechol (4-CC)

Name of the model compound	**4-chlorocatechol**
Synonym	4-chloropyrocatechol
IUPAC	4-chlorobenzene-1,2-diol
CAS No.	2138229
Molecular Formulae	$C_6H_5ClO_2$
Molecular weight	144.56
Melting Point	88 ^oC
Boiling point	140 ^oC
λ max	283 nm
Structure	

Photocatalytic degradation of 4-chlorocatechol (4-CC) in aqueous solution was studied in slurry mode employing photocatalysts such as TiO_2 or ZnO under UV/solar light in the presence of sodium hypochlorite as an oxidant. The effect of key

operating parameters on degradation efficiency (i.e. catalyst dose, pH, oxidant concentration) has been investigated.

4.3.1 Time dependent degradation of 4-CC

The time dependent UV-vis spectra of 4-chlorocatechol (4-CC) in aqueous solution (50 mg/L) is shown in Fig. 4.8. The absorption peak was observed at 283 nm which decreased gradually during photocatalysis, thus indicating the degradation of 4-CC over time with ZnO dose of 1.5 g/L at pH 8.

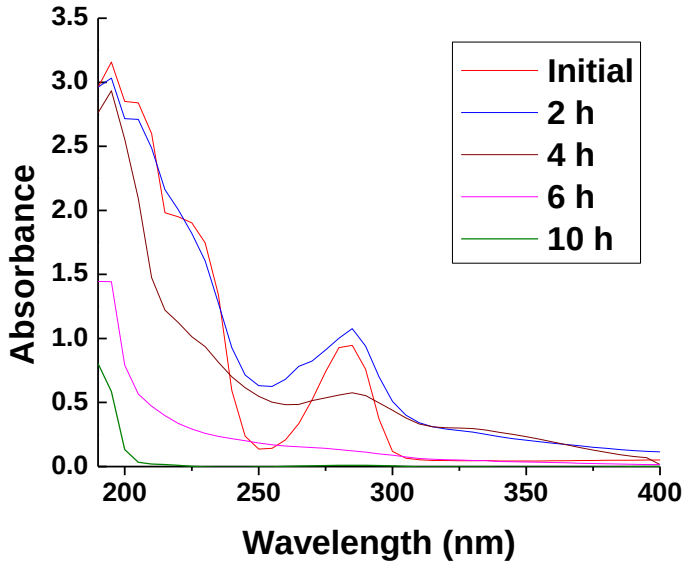


Fig. 4.8: Time dependent photocatalytic degradation of 4-CC (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; pH 8.0; Irradiation time: 10 h)

4.3.2 Photolysis/photocatalytic degradation of 4-CC

100 ml of 4-CC (50 mg/L) in aqueous solution having pH of 6.5 and catalyst dose of 2.5 g/L in case of TiO_2 and 1.5 g/L in case of ZnO were subjected to treatment under different experimental conditions as indicated in Figs. 4.9(a) & 4.9(b) respectively. The irradiation in the absence of photocatalyst showed limited degradation of 4-CC (9.8 %) over 6 h, whereas, in the presence of UV and photocatalyst, 87.4 and 98.6% degradation was achieved with TiO_2 and ZnO at 6 and 2 h respectively. When the adsorption studies of 4-CC (50 mg/L) were carried out

with TiO_2 and ZnO in the dark, it was found that 37.1% of 4-CC was adsorbed on to TiO_2 whereas 39.4% 4-CC adsorption was observed with ZnO.

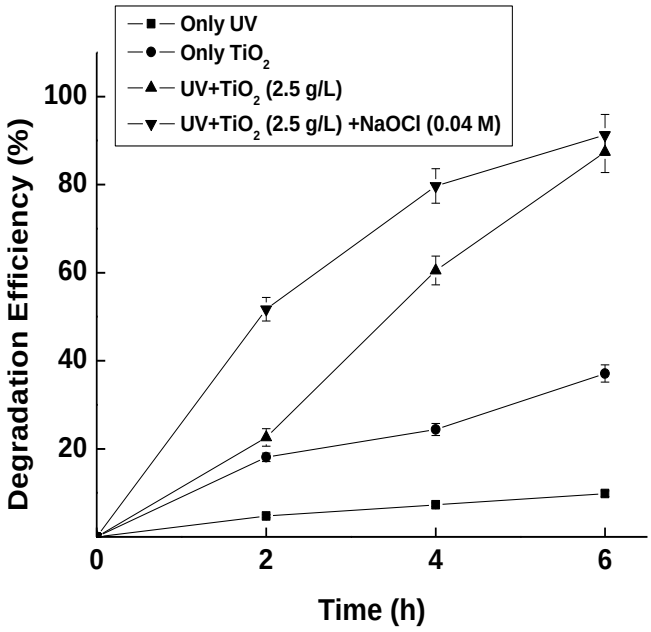


Fig. 4.9(a): Photolysis and photocatalytic (TiO_2) treatment of 4-CC (4-CC: 50 mg/L; TiO_2 dose: 2.5 g/L; pH 6.5; NaOCl: 0.04 M; Irradiation time: 6 h)

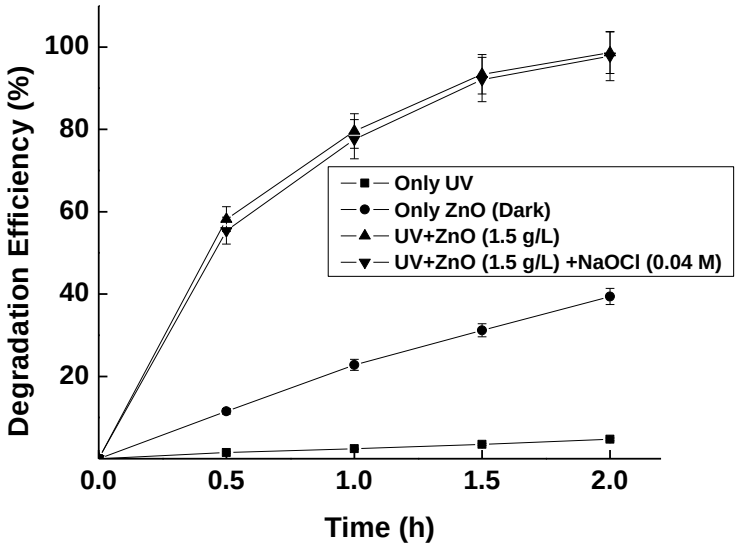


Fig. 4.9(b): Photolysis and photocatalytic (ZnO) treatment of 4-CC (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; pH 6.5; NaOCl: 0.04 M; Irradiation time: 2 h)

4.3.3 Degradation of 4-CC using TiO_2 as photocatalyst

The experiments were conducted to optimize the parameters associated with the degradation of 4-CC using TiO_2 as catalyst under UV irradiation. The parameters considered were catalyst dose, pH, and oxidant concentration. In order to optimize the process parameters for the degradation of 4-CC (50 mg/L), the photocatalytic experiments were performed by varying TiO_2 dose (1.0-3.0 g/L), pH (4-12) and NaOCl concentration (0.02-0.06 M). The graph (Fig. 4.10(a)) plotted between amount of catalyst used and the degradation efficiency reveals that maximum degradation of 87.4% was achieved with 2.5 g/L at pH (6.5) after 6 h of UV irradiation. However, increasing catalyst dose beyond 2.5 g/L reduced the extent of degradation to 62.7% with 3 g/L TiO_2. Figure 4.10(b) presents the observations for the effect of pH on degradation efficiency using TiO_2 (2.5 g/L) under UV light. The maximum photodegradation of 87.4% could be achieved at pH of 6.5. After optimizing the catalyst dose and pH, the effect of oxidant (NaOCl) concentration on the photodegradation efficiency was analyzed. Addition of sodium hypochlorite as an oxidant in the concentration range of 0.02 to 0.06 M along with TiO_2 (2.5 g/L) at pH of 6.5 was observed to improve the rate of photocatalytic degradation of 4-CC. The observations presented in Figure 4.10(c) indicated that the addition of 0.04 M NaOCl enhanced the rate constant or alternatively, reduced the time required to achieve same extent of degradation (91.6%). With a focus on reducing the operational cost of the process, further investigations were carried out using solar light. The aqueous suspensions of 4-CC (50 mg/L) was exposed to UV and solar light independently under optimized conditions (2.5g/L TiO_2, pH 6.5, 0.04 M NaOCl). The degradation efficiency was found to be higher in solar light (92.7%) as compared to 91.6% that was attained in UV light (**Fig. 4.10(d)**).

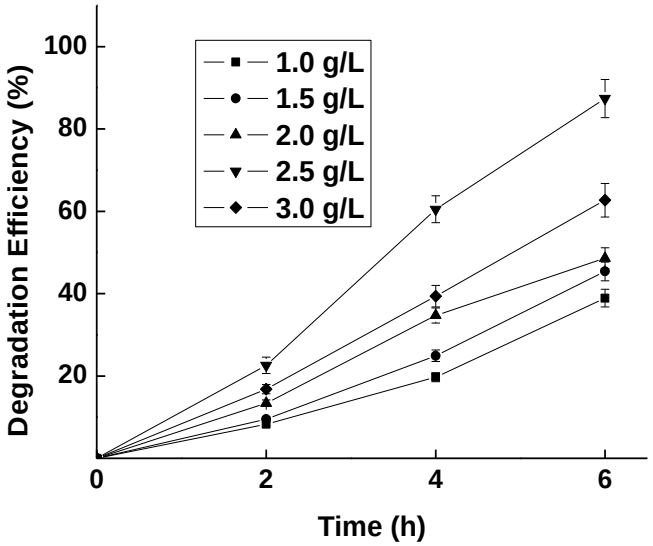


Fig. 4.10(a): Effect of TiO_2 dose on the degradation of 4-CC (4-CC: 50 mg/L; pH 6.5; Irradiation time: 6 h)

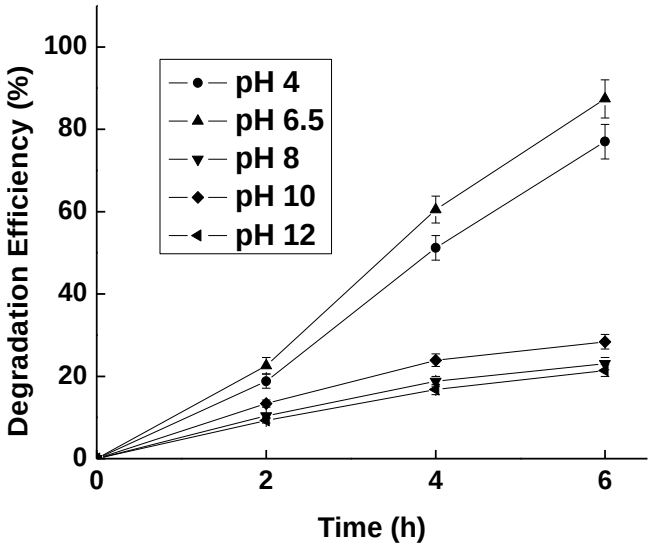


Fig. 4.10(b): Effect of pH on the degradation of 4-CC (4-CC: 50 mg/L; TiO_2 dose: 2.5 g/L; Irradiation time: 6 h)

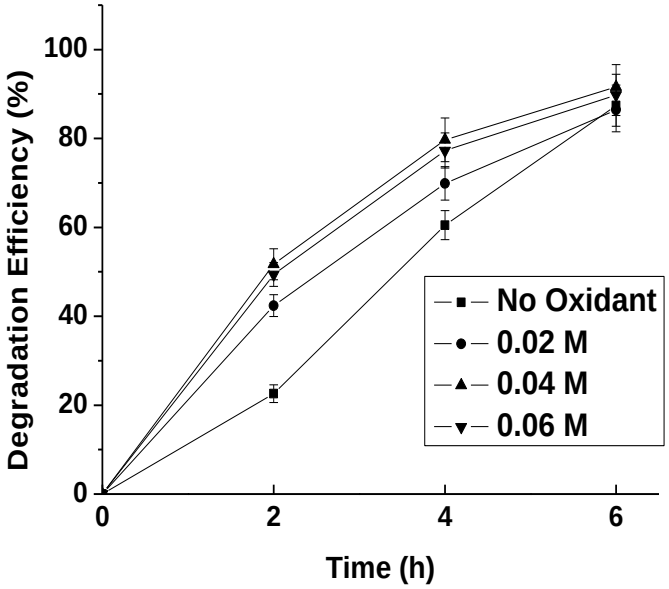


Fig. 4.10(c): Effect of oxidant concentration (NaOCl) on the degradation of 4-CC (4-CC: 50 mg/L; TiO_2 dose: 2.5 g/L; pH 6.5; Irradiation time: 6 h)

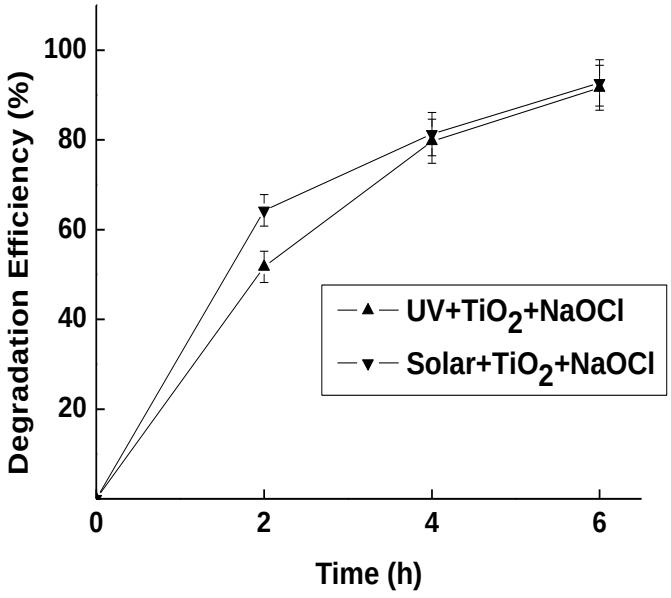


Fig. 4.10(d): Effect of UV/solar light on the degradtion of 4-CC (4-CC: 50 mg/L; TiO_2 dose: 2.5 g/L; pH 6.5; Irradiation time: 6 h)

4.3.4 Degradation of 4-CC using ZnO as photocatalyst

The parametric optimization of 4-CC employing ZnO as catalyst was performed in order to adjudge the most favourable conditions for photocatalytic treatment. In order to assess the effect of catalyst loading, the experiments were performed by varying the ZnO dose from 1.0 to 3.0 g/L for 4-CC concentration of 50 mg/L at pH 6.5 under UV irradiation. The maximum degradation efficiency of 82.8% was obtained with ZnO dose (1.5 g/L) after 2 h of UV exposure (Fig. 4.11(a)). However, further increase in dosage of catalyst decreased the degradation efficiency to 82.1 and 80.5% with 2.0 and 2.5 g/L ZnO, respectively. Therefore, 1.5 g/L was selected as the optimum dose of ZnO for further experiments. The role of pH in the rate of photocatalytic degradation of 4-CC was studied in the pH range of 4 to 12. Observations indicated pronounced influence of pH on the degradation of 4-CC. A significant increase in the extent of photodegradation (98.6%) was achieved with ZnO (1.5 g/L) at pH 8.0 after 2 h as depicted in Fig. 4.11(b). However, the presence of oxidant (sodium hypochlorite) with ZnO (1.5 g/L) at pH 8 did not result in enhancement of degradation efficiency of 4-CC (Fig. 4.11(c)). The effect of light sources (UV/solar light) were assessed on the degradation of 4-CC (50 mg/L) under optimized conditions (ZnO 1.5 g/L, pH 8) by exposing 4-CC solution to UV and solar light independently. The solar induced photocatalytic process resulted in degradation of 99.1% in comparison to 98.6% degradation that was achieved in UV light (Fig. 4.11(d)). The results depict better efficacy of solar light over UV in facilitating photocatalytic degradation of 4-CC.

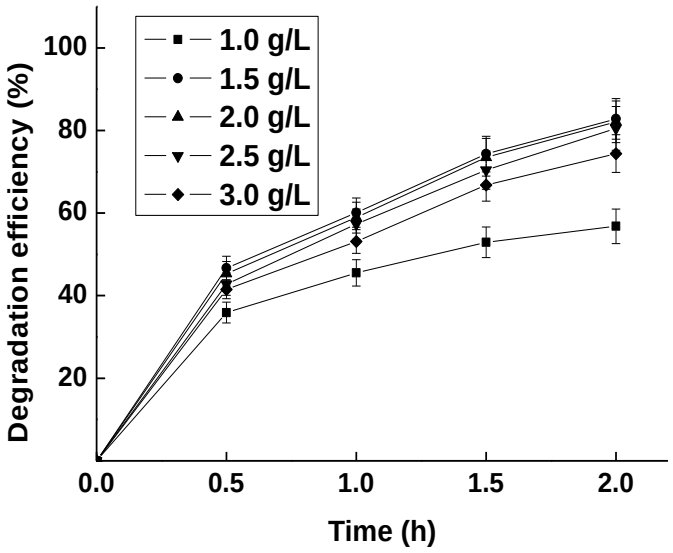


Fig. 4.11(a): Effect of ZnO dose on the degradation of 4-CC (4-CC: 50 mg/L; pH 6.5; Irradiation time: 2 h)

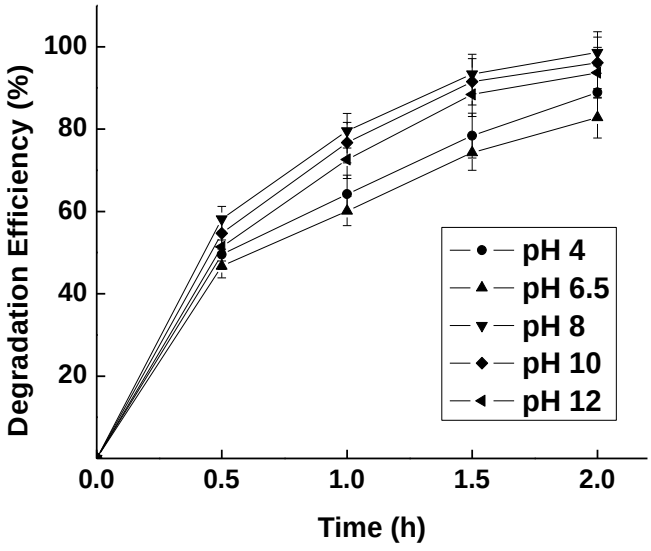


Fig. 4.11(b): Effect of pH on the degradation of 4-CC (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; Irradiation time: 2 h)

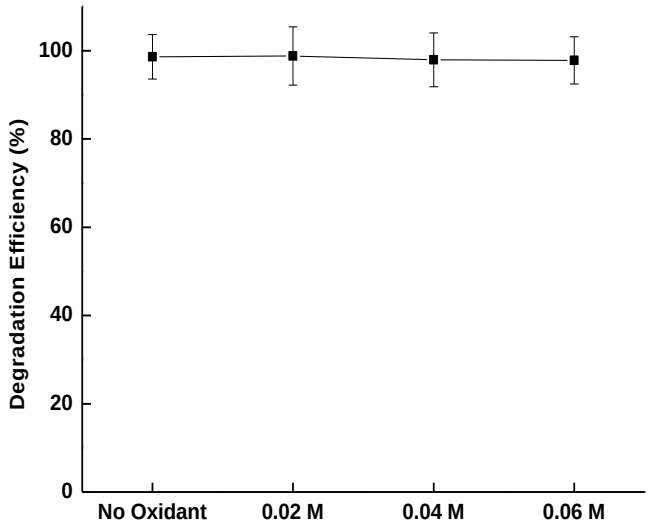


Fig. 4.11(c): Effect of oxidant (NaOCl) concentration on the degradation of 4-CC (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; pH 8.0; Irradiation time: 2 h)

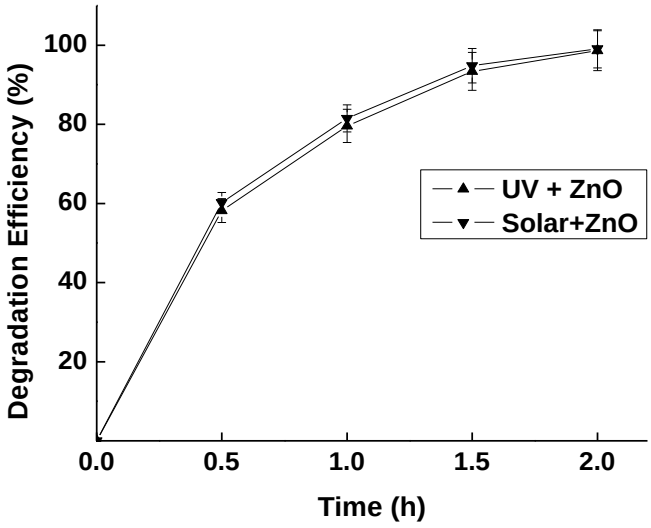


Fig. 4.11(d): Effect of UV/solar light on the degradation of 4-CC (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; pH 8.0; Irradiation time: 2 h)

4.3.5 Kinetics of degradation

To understand the kinetics of degradation of 4-CC, the order of reaction and the apparent rate constant of the 4-CC degradation were determined. The value of apparent rate constants of 4-CC degradation has been shown in Table 4.6 which was determined from the slope of straight line of the graph **(**Fig. 4.12(a) and Fig. 4.12(b)) between ln $[4\text{-CC}]_O/[4\text{-CC}]$ versus time. The results reveal that the 4-CC degradation

was higher with ZnO as compared to TiO_2. Moreover, the degradation of 4-CC is in agreement with a pseudo first-order kinetics of Langmuir-Hinshelwood model.

Table: 4.6. Apparent first-order rate constants for degradation of 4-CC

Catalyst	$K_{app(4\text{-}CC)}$ (h^{-1})	r^2
ZnO	1.036	0.975
TiO_2	0.689	0.923

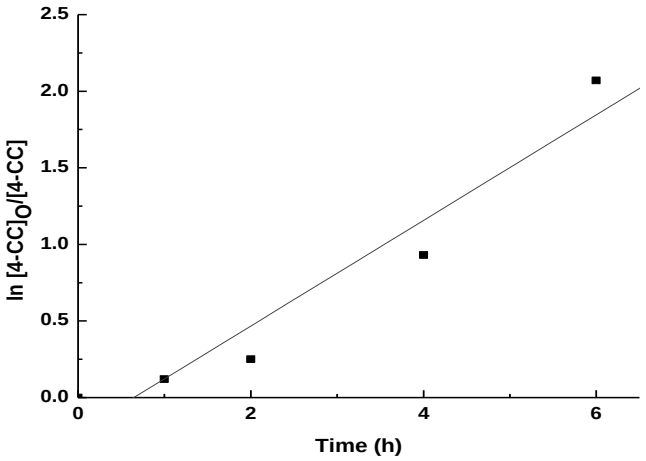


Fig. 4.12(a): Linear regression on TiO_2 induced degradation of 4-CC w.r.t. time (4-CC: 50 mg/L; TiO_2 dose: 2.5 g/L; pH 6.5; Irradiation time: 6 h)

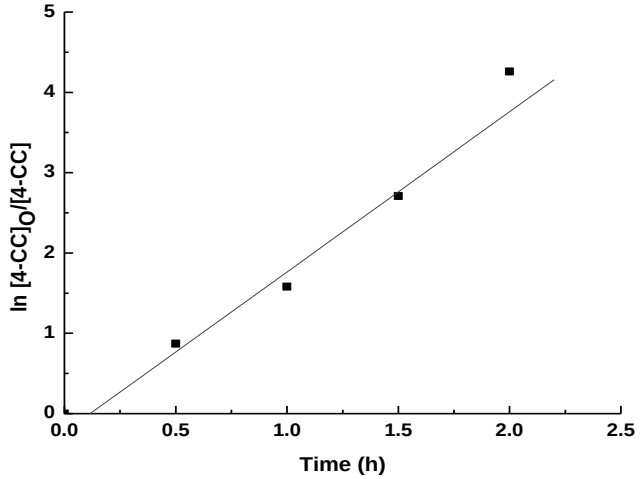


Fig. 4.12(b): Linear regression on ZnO induced degradation of 4-CC w.r.t. time (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; pH 8.0; Irradiation time: 2 h)

4.3.6 HPLC studies

High performance liquid chromatography studies were carried out to confirm the degradation of 4-CC (50 mg/L**)** with ZnO induced photodegradation under optimized conditions (ZnO dose: 1.5 g/L, pH 8.0). Fig. 4.13(a) shows the HPLC chromatogram of aqueous solution of 4-CC (50 mg/L) which depicts the characteristic peak of the model compound at retention time of 3.57 min. The results shown in Fig. 4.13(b) indicate the decrease in the peak corresponding to 4-CC, which further confirmed its degradation. Few intermediates were observed to appear during the photocatalytic treatment.

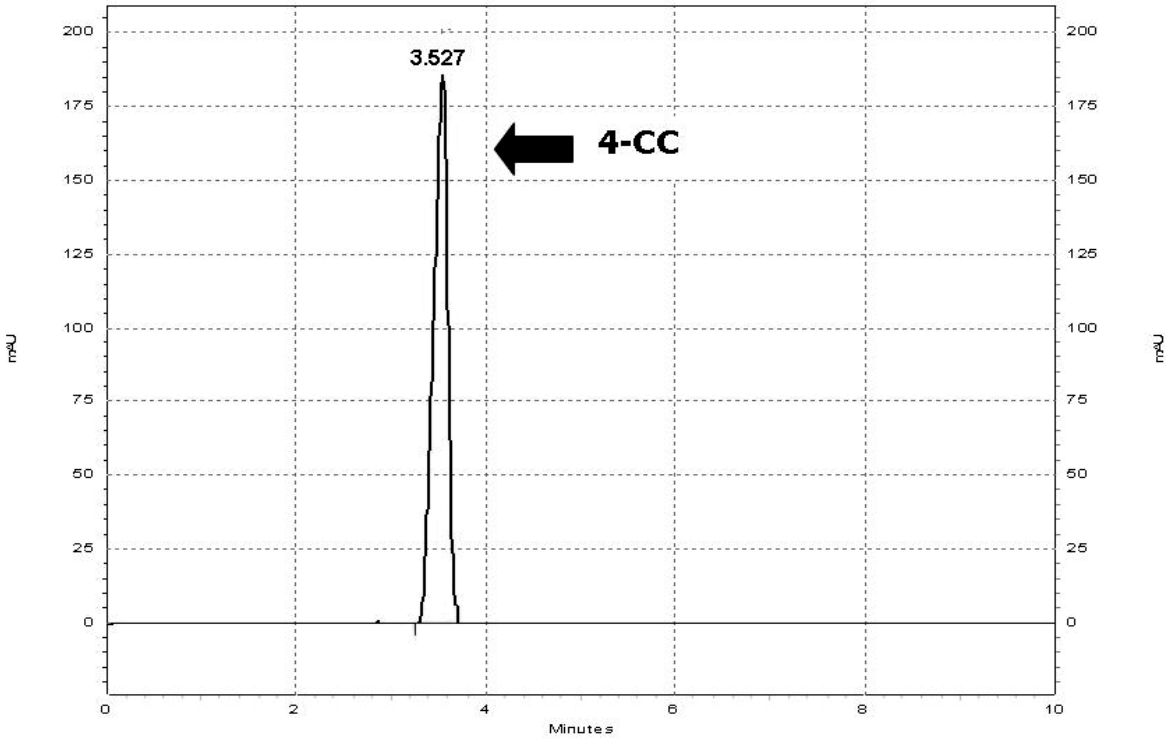


Fig. 4.13(a): HPLC of 4-chlorocatechol aqueous solution

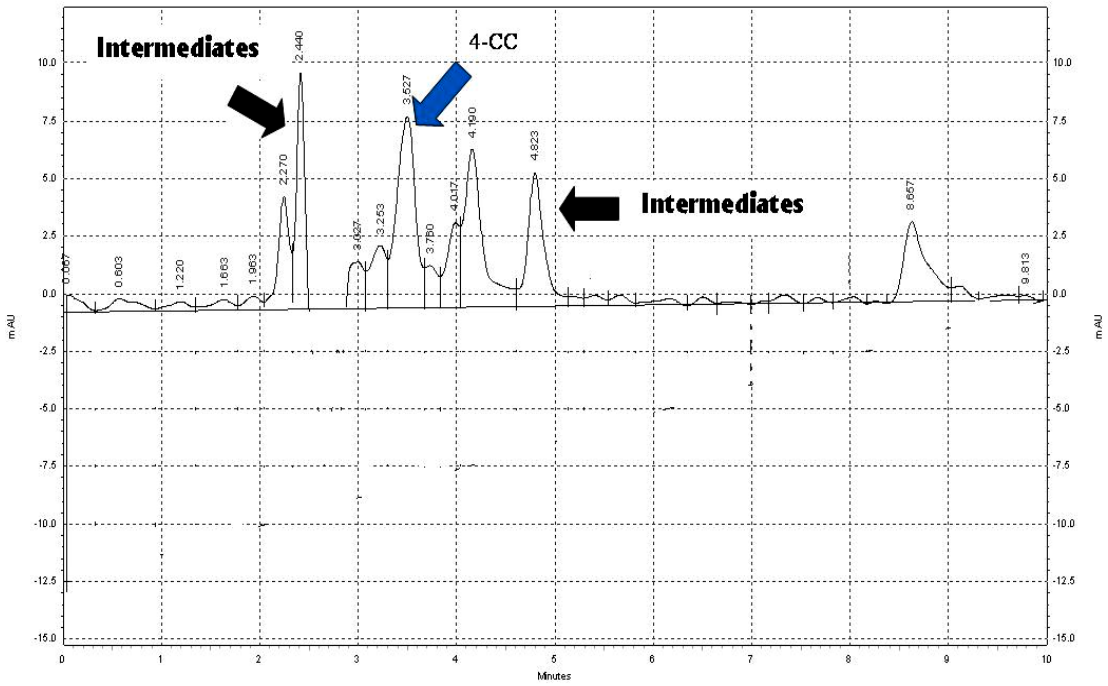
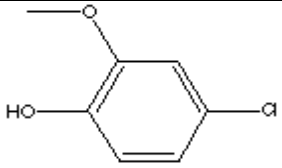


Fig. 4.13(b): HPLC of 4-CC after 2 h of photocatalytic treatment (4-CC: 50 mg/L; ZnO dose: 1.5 g/L; pH 8.0)

4.4 PHOTOCATALYTIC DEGRADATION OF 4-CHLOROGUAIACOL

4-chloroguaiacol (4-CG) is a clear, faint brown liquid usually found in bleach mill effluents. 4-CG was purchased from Sigma Aldrich, USA and used without further purification. 4-CG is a strong transparent liquid of unpleasant odour and it is slightly soluble in water. 4-CG is a corrosive poison that absorbs by contact with skin, by inhalation or by ingestion. In 4-CG, -OCH_3 group is non polar so it is insoluble in water, but soluble in ethanol due to the presence of –OH group. Due to its low solubility in aqueous solution, it was first dissolved in 2 ml of ethanol and then subsequently in double distilled water. 4-CG is a versatile intermediate in chemical syntheses because both the hydroxyl group and the aromatic ring can react by both electrophilic and nucleophilic substitution. The physical properties and chemical structure of 4-CG are given in Table 4.7.

Table: 4.7. Characteristics of 4-chloroguaiacol (4-CG)

Name of the model compound	**4-chloroguaiacol**
Synonym	p-chloroguaiacol; 4-chloropyrocatechol monomethyl ether
IUPAC	4-chloro-2-methoxy phenol
CAS No.	16786
Molecular Formulae	$C_7H_7ClO_2$
Molecular weight	158.58
Boiling point	241 ^oC
Flash Point	100 ^oC
Density	1.304 g/cm^3
λ_{max}	281.5 nm
Structure	

Keeping in view the presence of 4-CG in the bleach mill effluents and the limited studies on the degradation of 4-chloroguaiacol (4-CG), the photocatalytic degradation of 4 CG was investigated using TiO_2/ZnO as photocatalyst employing UV/solar light along with sodium hypochlorite as an oxidant. The effect of various photocatalytic process parameters and reaction kinetics were examined.

4.4.1 Time and concentration dependent degradation of 4-CG

The typical time dependent UV-Vis spectra of 4-CG (25 mg/L) in aqueous solution is shown in Fig. 4.14(a). The absorption peaks at 230.0 and 281.5 nm were observed to decrease gradually during photocatalysis with ZnO indicating the gradual degradation of the compound. Experiments were conducted at different concentration of 4-CG viz. 10, 25, 50 and 100 mg/L with catalyst dose of 2 g/L ZnO at pH 10 to assess the effect of initial substrate concentration on the degradation efficiency. The

results depict that degradation efficiency decreased with increase in the substrate concentration (Fig. 4.14 (b)). At low 4-CG loading (10 mg/L), about 100% degradation of the pollutant was achieved in 4 h while 92.7% degradation was achieved in 6 h when 25 mg/L was used. When 50 and 100 mg/L of initial 4-CG loadings were used for the same time window of 6 h, degradations were 83.4 and 64.3%, respectively.

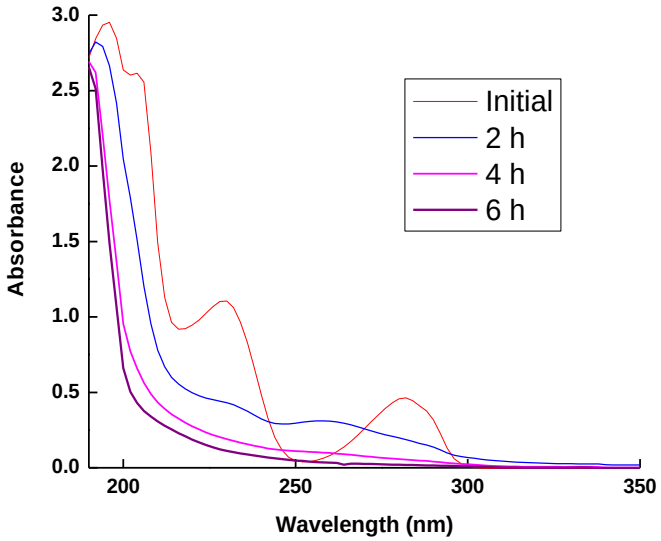


Fig. 4.14(a): Time dependent photocatalytic degradation of 4-CG (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 6 h)

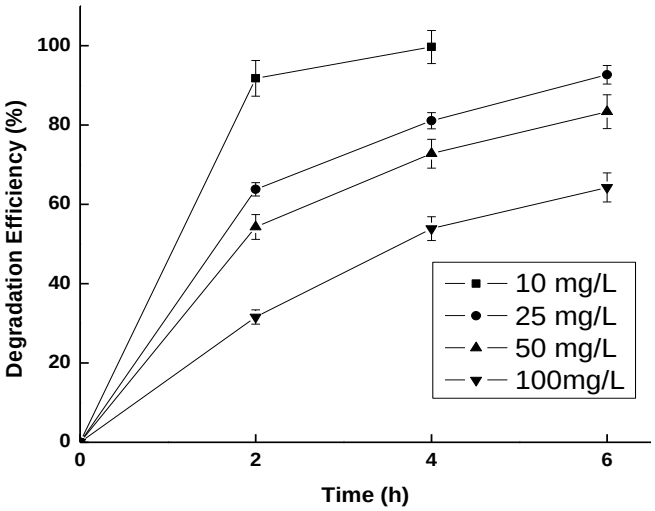


Fig. 4.14(b): Effect of initial concentration of 4-CG on the degradation efficiency (ZnO dose: 2 g/L; pH 10; Irradiation time: 6 h)

4.4.2 Photolysis/photocatalytic degradation of 4-CG

4-CG (25 mg/L) in aqueous solutions was subjected to treatment under UV light alone and UV light in the presence of TiO_2 (2 g/L) or ZnO (2 g/L) as photocatalyst (Fig. 4.15). The irradiation in the absence of photocatalyst showed very little degradation of 4-CG (9 %) in 6 h, whereas, in the presence of UV and photocatalyst, 47.6 and 92.7% degradation was achieved in 6 h with TiO_2 (6.75 pH) and ZnO (10 pH), respectively. When the adsorption studies of 4-CG (25 mg/L) were carried out with TiO_2 and ZnO in the dark, it was found that after 6 h duration, 16 % of 4-CG was adsorbed on to TiO_2 whereas 21% 4-CG adsorption was observed with ZnO.

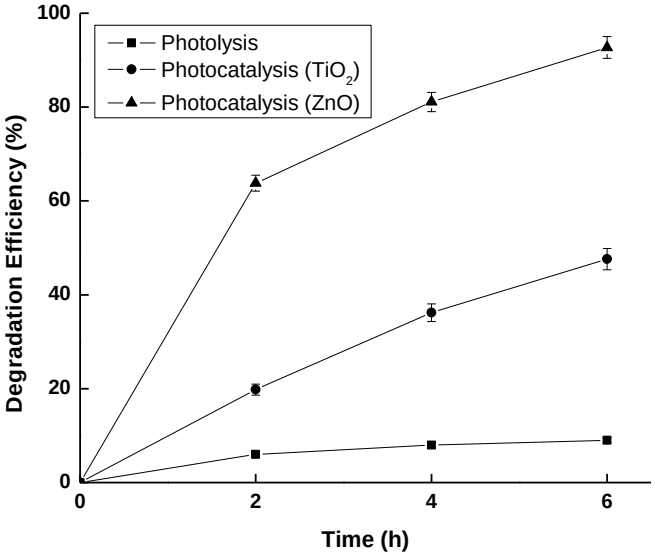


Fig. 4.15: Photolysis and photocatalytic degradation of 4-CG (4-CG: 25 mg/L; TiO_2 dose: 2 g/L; pH 6.75 & ZnO dose: 2g/L; pH 8.0; Time: 6 h)

4.4.3 Degradation of 4-CG using TiO_2 as photocatalyst

In order to optimize the process parameters for the degradation of 4-CG (25 mg/L), the photocatalytic experiments were performed by varying TiO_2 dose (1.5-3.0 g/L), pH (2-12) and NaOCl concentration (0.01-0.04 M). The graph plotted between amount of catalyst used and the degradation efficiency reveals that maximum

degradation of 47.6% was achieved with 2 g/L at pH (6.75) after 6 h of UV irradiation as shown in Fig 4.16(a). However, increasing catalyst dose beyond 2 g/L, reduced the extent of degradation to 28.4% with 3 g/L TiO_2 dose. Fig 4.16(b) represents the observations on the effect of pH on degradation efficiency using TiO_2 (2 g/L) under UV light. The maximum photodegradation of 47.6% was achieved with TiO_2 at pH 6.75. Hence, pH of 6.75 was chosen as an optimum pH for further experimentation. After optimizing the catalyst dose and pH, the effect of oxidant (NaOCl) concentration on the photodegradation efficiency was analyzed. The presence of oxidant lead to increase in the rate of degradation in the initial phase; however the extent of degradation was almost same after 6 h of irradiation as depicted in Figure 4.16(c). Blank experiments were conducted by irradiating the aqueous solution of organic compound in the absence of photocatalyst using optimum concentration of oxidant and no observable loss of the compound was noticed during irradiation.

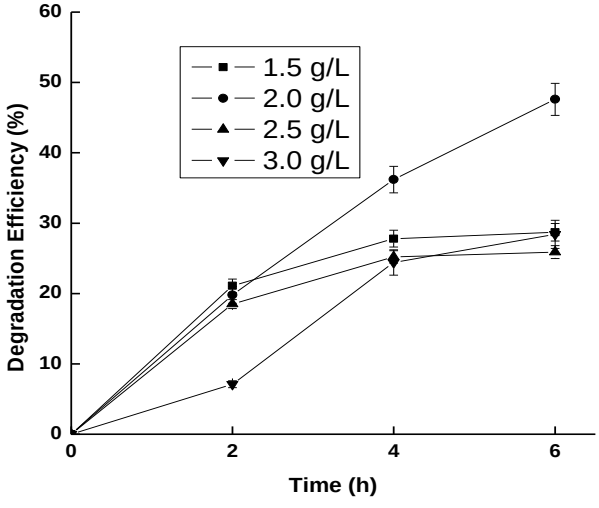


Fig. 4.16(a): Effect of TiO_2 dose on the degradation of 4-CG (4-CG: 25 mg/L; pH 6.75; Irradiation time: 6 h)

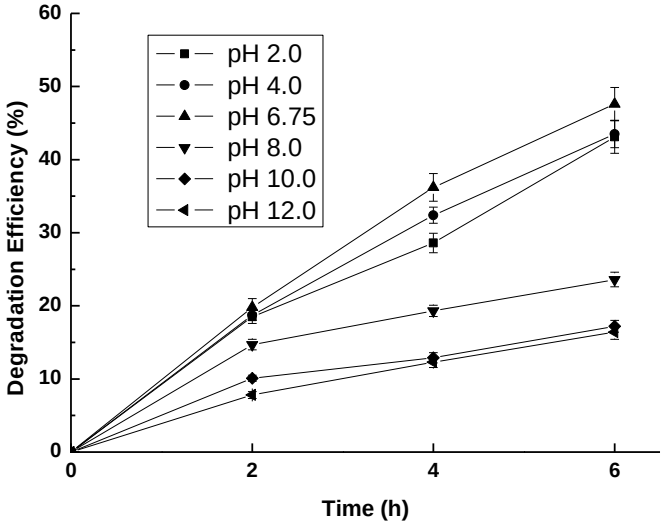


Fig. 4.16(b): Effect of pH on the degradation of 4-CG (4-CG: 25 mg/L; TiO_2 dose: 2 g/L; Irradiation time: 6 h)

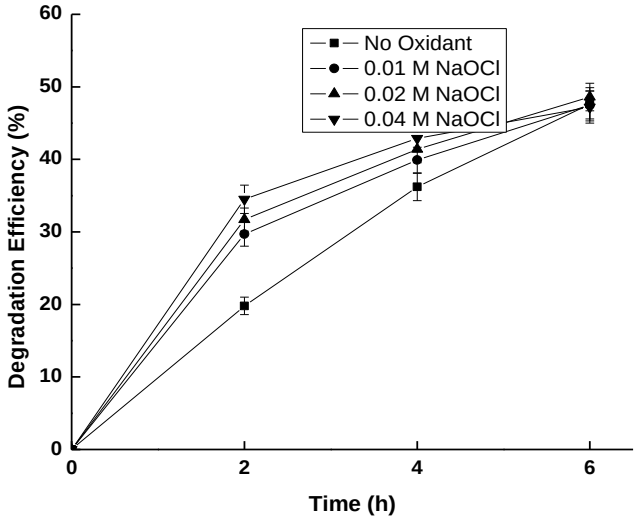


Fig. 4.16(c): Effect of oxidant concentration (NaOCl) on the degradation of 4-CG (4-CG: 25 mg/L; TiO_2 dose: 2 g/L; pH 6.75; Irradiation time: 6 h)

In order to assess the efficacy of process in solar light, the aqueous suspensions of 4-CG (25 mg/L) under optimized conditions (TiO_2 2 g/L, pH 6.75) were exposed to UV and solar light independently. The degradation was 36.9% in solar light as compared to 47.6% in UV light (Figure 4.16(d)).

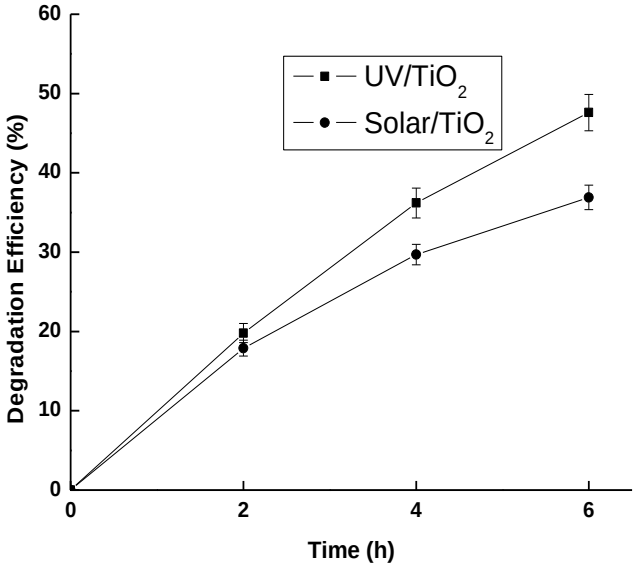


Fig. 4.16(d): Effect of UV/solar light on the degradation of 4-CG (4-CG: 25 mg/L; TiO_2 dose: 2 g/L; pH 6.75; Irradiation time: 6 h)

4.4.4 Degradation of 4-CG using ZnO as photocatalyst

The parametric optimization of 4-CG employing ZnO as catalyst under UV light was performed in order to determine the favourable conditions for photocatalytic treatment. In order to assess the effect of catalyst loading, the experiments were performed by varying the ZnO dose from 1.5 to 3.0 g/L for 4-CG concentration of 25 mg/L at pH 6.75 and UV irradiation for 6 h. The degradation efficiency increased to 75.4% with increase in ZnO loading, especially up to 2 g/L and reduced to 68.3% with 2.5 g/L ZnO dose (Fig. 4.17(a)). Therefore, 2 g/L was selected as the optimum dose of ZnO for further experiments. Further, the role of pH in the rate of photocatalytic degradation of 4-CG was studied in the pH range of 2.0 to 12.0. The maximum photodegradation (92.7%) was obtained with ZnO (2 g/L) at pH 10 (Fig. 4.17(b)). Addition of sodium hypochlorite as an oxidant along with ZnO (2 g/L) at pH 10 did not show any improvement in photocatalytic degradation of 4-CG. Fig. 4.17(c) shows that oxidant addition showed no effect on the rate constant. The effect of light sources (UV/solar light**)** were assessed on the degradation of 4-CG (25 mg/L) under

optimized conditions (ZnO 2 g/L, pH 10) by exposing 4-CG solution to UV and solar light independently. Fig 4.17(d) shows that the rate of degradation, under optimized conditions was marginally higher (94.2%) under solar light as compared to 92.7% in UV light after 6 h of irradiation exposure.

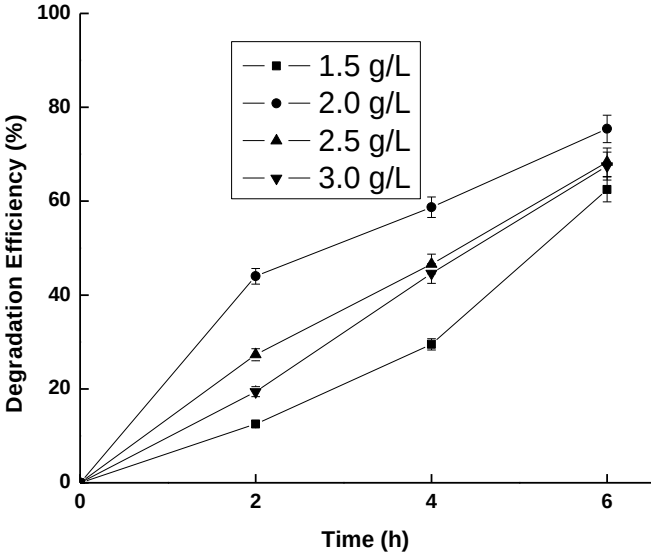


Fig. 4.17(a): Effect of ZnO dose on the degradation of 4-CG (4-CG: 25 mg/L; pH 6.75; Irradiation time: 6 h)

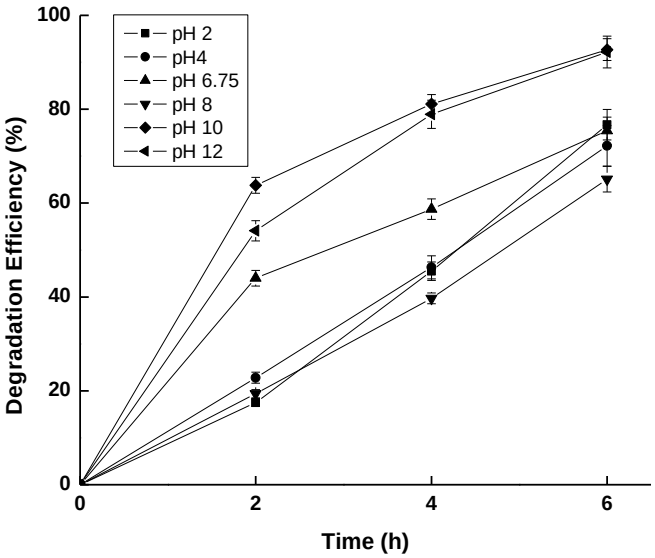


Fig. 4.17(b): Effect of pH on the degradation of 4-CG (4-CG: 25 mg/L; ZnO dose: 2 g/L; Irradiation time: 6 h)

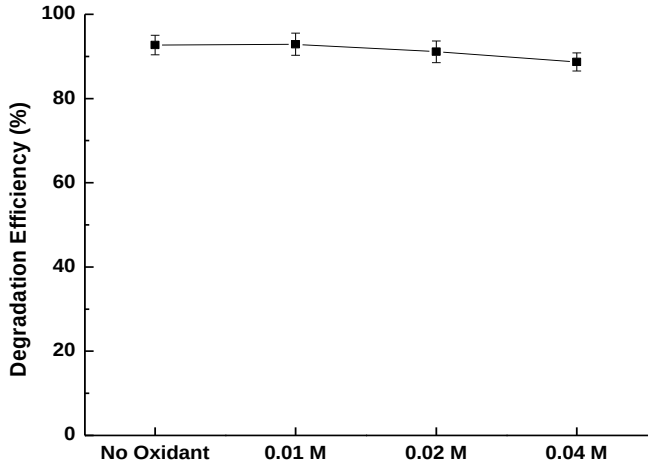


Fig. 4.17(c): Effect of oxidant concentration (NaOCl) on the degradation of 4-CG (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 6 h)

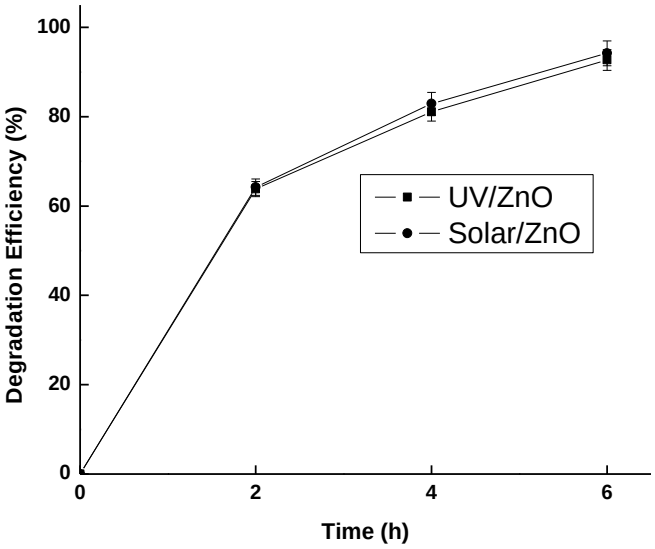


Fig. 4.17(d): Effect of UV/solar light on the degradation of 4-CG (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 6 h)

4.4.5 Kinetics of degradation

A plot of $\ln[4\text{-CG}]_0/[4\text{-CG}]$ vs. time as shown in Fig. 4.18(a) & 4.18(b) in case of TiO_2 and ZnO represents straight line with values of apparent rate constants and linear regression coefficients given in Table 4.8. The results reveal that the rate constant for degradation of 4-CG was more with ZnO as compared to TiO_2 which implies that ZnO was more effective in the degradation of 4-CG as compared to TiO_2.

The straight lines as obtained were in agreement with a pseudo first-order degradation of 4-CG concentration.

Table: 4.8. Apparent first-order rate constants for degradation of 4-CG

Catalyst	$K_{app(4\text{-}CG)}$ (h^{-1})	R^2
ZnO	0.447	0.995
TiO_2	0.115	0.996

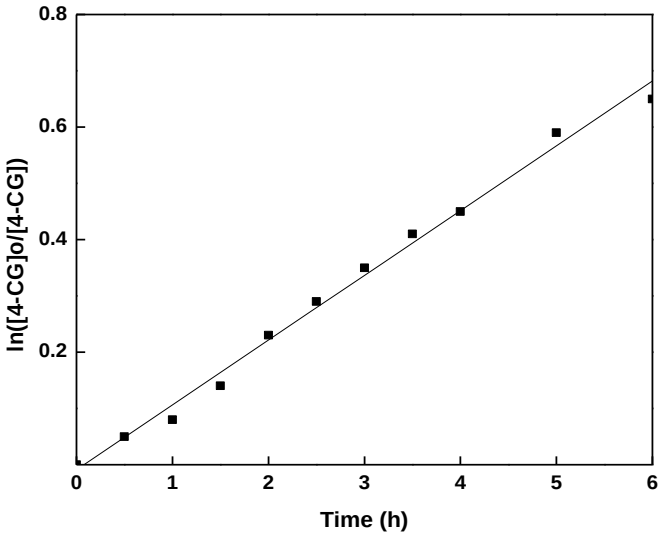


Fig. 4.18(a): Linear regression on TiO_2 induced degradation of 4-CG w.r.t. time (4-CG: 25 mg/L; TiO_2 dose: 2 g/L; pH 6.75; Irradiation time: 6 h)

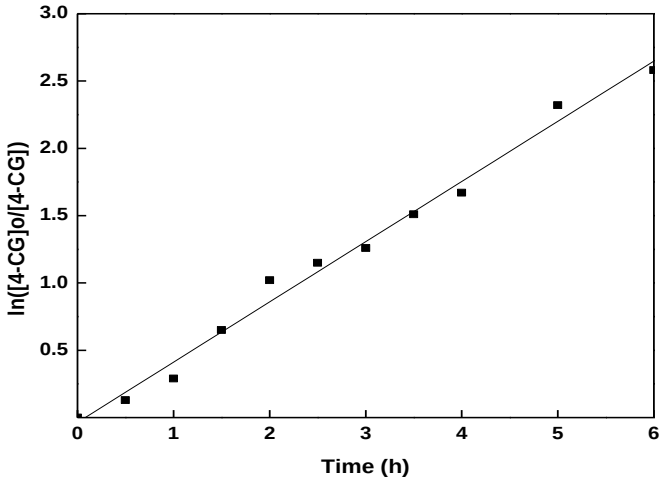


Fig. 4.18(b): Linear regression on ZnO induced degradation of 4-CG w.r.t. time (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 6 h)

4.4.6 Tracking the degradation of 4-CG

The degradation of 4-CG with photocatalysis was further confirmed by measuring reduction of characteristic peak in high performance liquid chromatography (HPLC). HPLC studies were carried out for the degradation of 4-CG with ZnO photocatalysis under optimized conditions (2 g/L ZnO, pH 10) for 6 h of solar irradiations.

High performance liquid chromatography studies were carried out to confirm the degradation of 4-CG with UV induced ZnO photocatalysis under optimized conditions (ZnO 2 g/L, pH 10). Fig. 4.19(a) shows the HPLC chromatogram of aqueous solution of 4-CG (25 mg/L) which depicts the characteristic peak of the model compound at retention time of 5.1 min. The results shown in Fig. 4.19(b) to 4.19(f) indicate the decrease in the peak corresponding to 4-CG, which further confirmed its degradation. One intermediate was observed to appear at retention time of 2.8 min. The concentration of this intermediate was observed to increase over time.

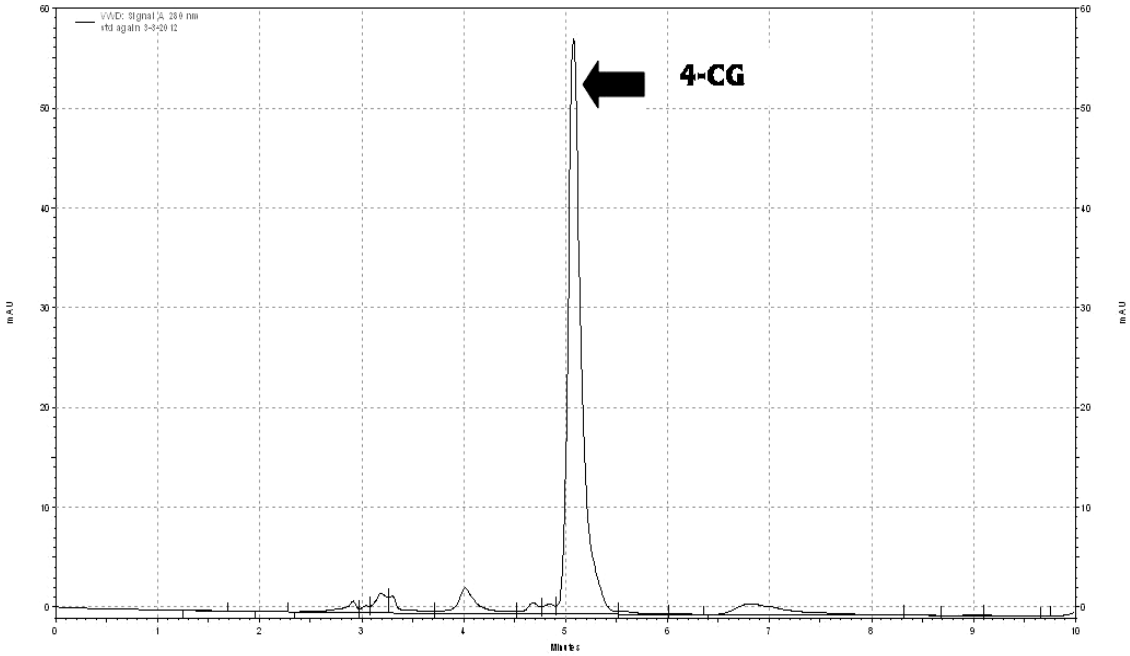


Fig. 4.19(a): HPLC of 4-chloroguaiacol aqueous solution

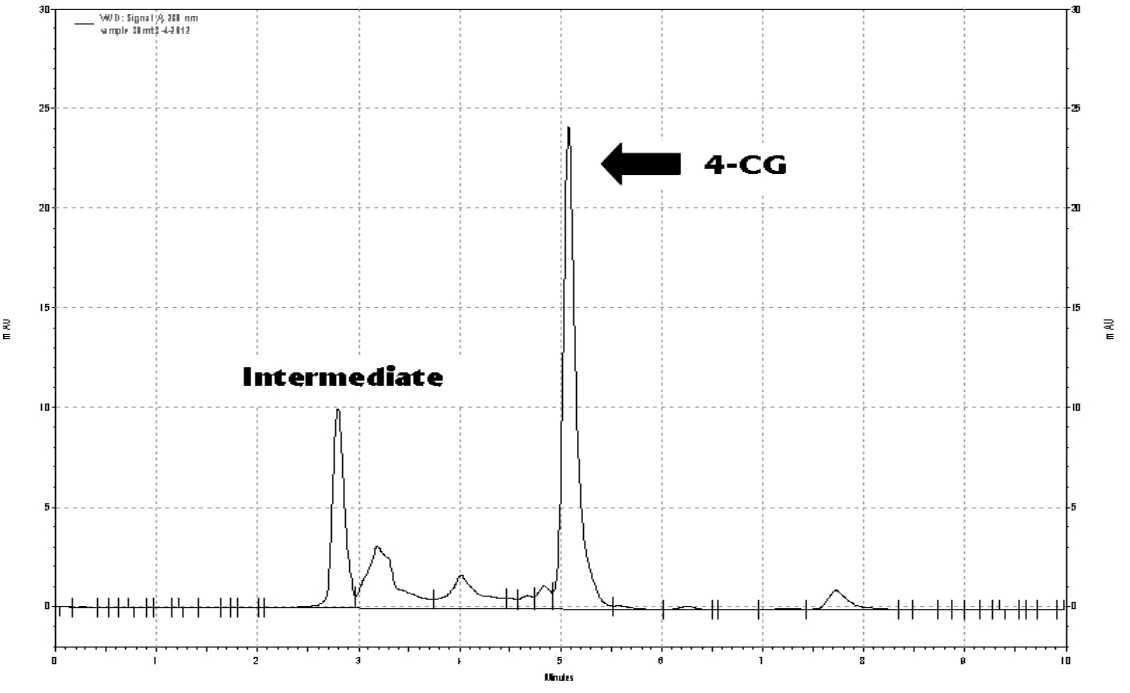


Fig. 4.19(b): HPLC of 4-CG after 0.5 h of photocatalytic treatment (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 0.5 h)

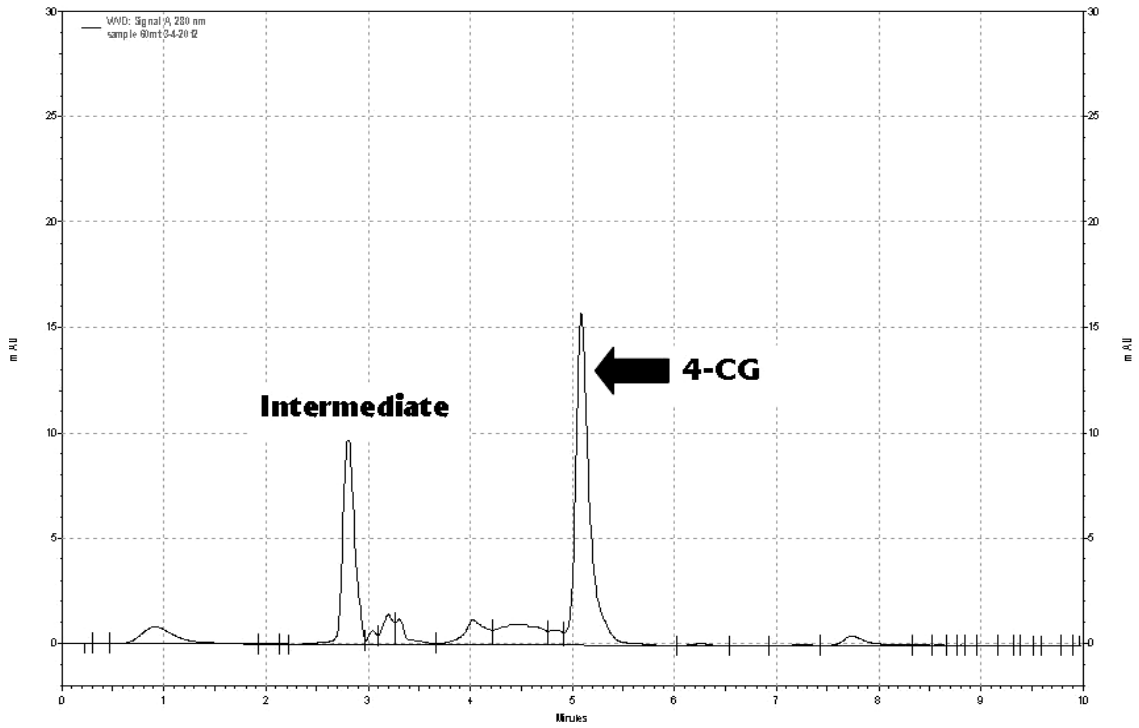


Fig. 4.19(c): HPLC of 4-CG after 1.0 h of photocatalytic treatment (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 1.0 h)

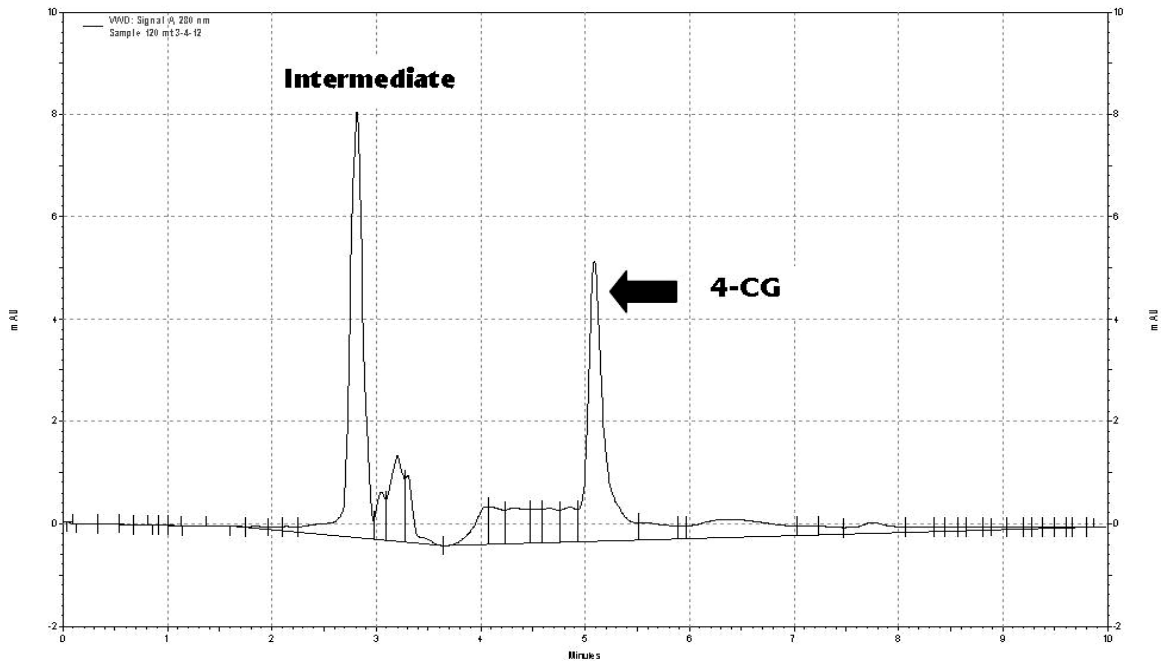


Fig. 4.19(d): HPLC of 4-CG after 2.0 h of photocatalytic treatment (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 2.0 h)

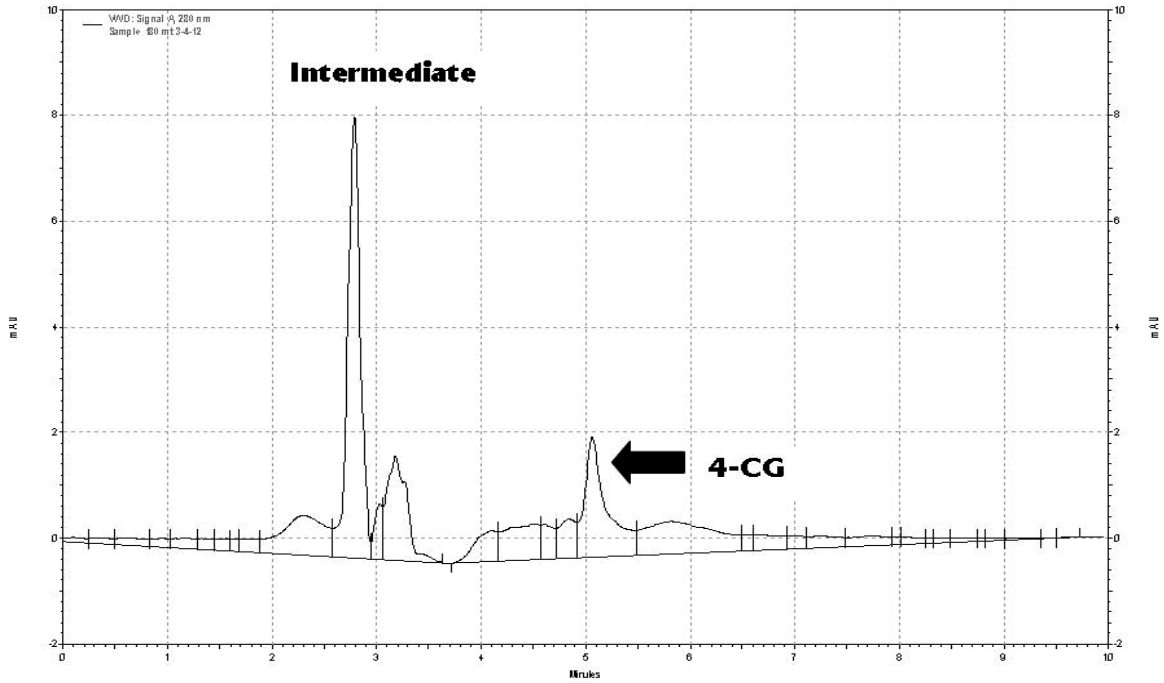


Fig. 4.19(e): HPLC of 4-CG after 3.0 h of photocatalytic treatment (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 3.0 h)

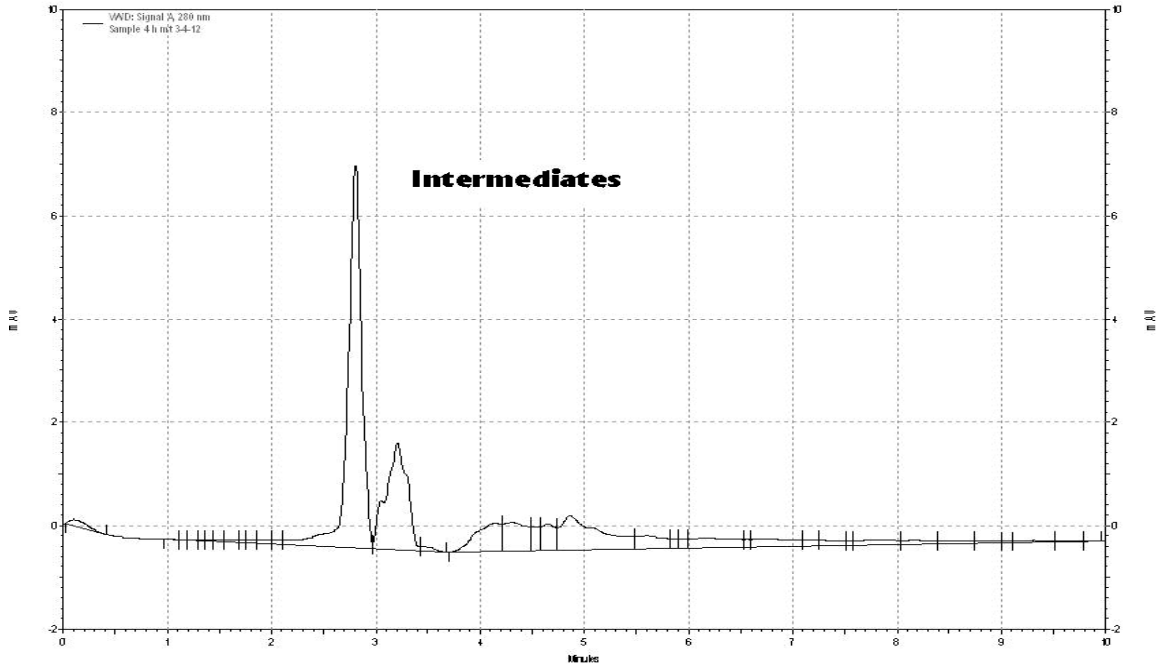


Fig. 4.19(f): HPLC of 4-CG after 4.0 h of photocatalytic treatment (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 4.0 h)

4.4.7 Assessing the efficacy of the recycled catalyst

The catalyst lifetime is an important parameter for economic viability of photocatalysis at industrial level. For photocatalytic treatment, catalyst recycling is one of the major challenges towards the large scale applications. 4-CG was subjected to degradation with recycled catalyst (ZnO) for 4 runs under optimized conditions (2 g/L ZnO, pH 10, UV irradiation time 6 h). After each run, the catalyst was recovered by filtration and activated at 105^0C and again used in photocatalytic treatment to study its recyclability. The results as shown in Fig. 4.20 depict that the catalyst could be effectively recycled for at least four times for facilitating the degradation of 4-CG wherein, the degradation efficiency decreased from 92.7 to 42.9% after four cycles.

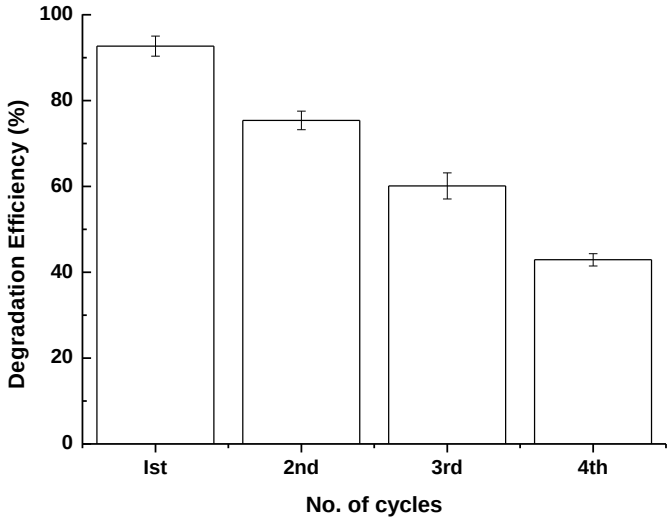


Fig 4.20: Recycling of catalyst (ZnO) in the degradation of 4-CG (4-CG: 25 mg/L; ZnO dose: 2 g/L; pH 10; Irradiation time: 6 h)

4.5 PHOTOCATALYSIS USING MIXED/ HETERO-STRUCTURED NANOPHOTOCATALYST SYSTEM

In order to explore the efficacy of mixed photocatalyst system, 4-CG was subjected to degradation with photocatalyst system comprising of mixture of ZnO and TiO_2. Alternatively, heterostructured nanophotocatalyst comprising 90% ZnO and

10% TiO_2 was synthesized, characterized and its photocatalytic activity was also evaluated for degradation of 4-CG.

4.5.1 Photocatalytic degradation of 4-CG using mixed photocatalysts

The photocatalytic efficacy of mixed catalysts were examined by mixing TiO_2 and ZnO in different proportions of 90:10, 70:30, 50:50, 30:70 and 10:90, using 4–CG (25 mg/L) as model compound. Photocatalytic experiments were performed with catalyst dose of 2 g/L of various catalysts – ZnO, TiO_2 independently as well as in combinations mixed in above mentioned ratios at pH 10. The rate of degradation was comparatively higher with ZnO as compared to TiO_2 when used independently. However, when the photocatalysts were mixed, better degradation efficiency was achieved as compared to the individual catalyst **(**Fig. 4.21**)**. The maximum degradation of 95.8% was observed when ZnO and TiO_2 were mixed in the ratio, 9:1 (ZnO: TiO_2), showing synergistic effect of TiO_2 at low concentration in combination with ZnO.

The photoassisted degradation of 4-CG was also carried out using 9:1/ ZnO: TiO_2 as photocatalyst and solar irradiation as light source. Fig. 4.22 illustrates the results of photodegradation of 4-CG using optimized conditions as a function of irradiation time under UV/solar light. The results indicate that the degradation of 4-CG was nearly similar with solar light as well as UV light wherein, 97.2% degradation efficiency was observed in 6 h of irradiation time under solar light, as compared to 95.8% degradation efficiency in the presence of UV irradiation for the same duration.

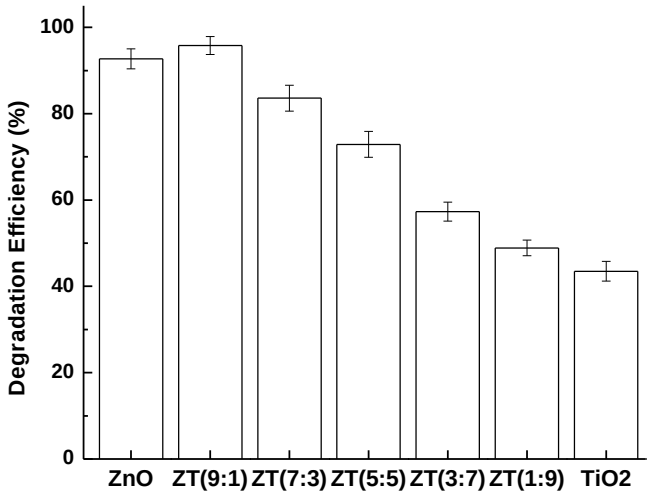


Fig. 4.21: Degradation efficiency of 4-CG with varying proportions of mixed catalysts (4-CG: 25 mg/L; Catalyst Dose: 2g/L; pH 10; Irradiation time: 6 h)

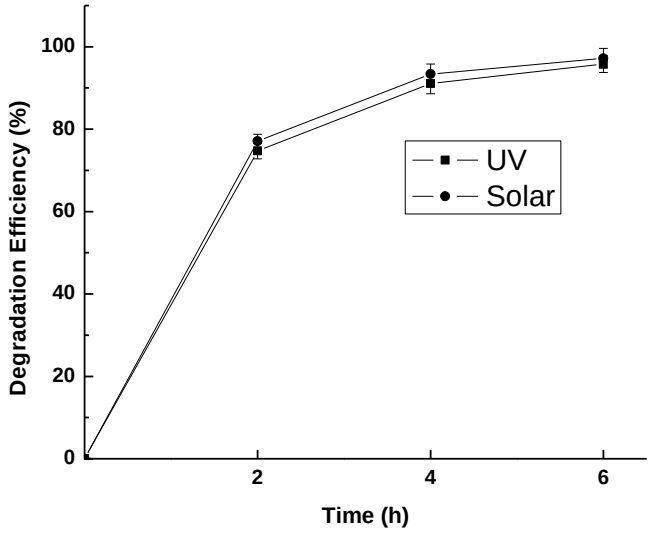


Figure 4.22: Degradation of 4-CG with mixed photocatalysts (4-CG: 25 mg/L; Mixed catalyst Dose: 2g/L; pH 10; Irradiation time: 6 h)

4.5.2 Photocatalytic degradation of 4-CG using synthesized heterostructured nano-photocatalysts

The heterostructured ZnO/TiO_2 nanophotocatalysts was prepared in molar ratio of 9:1 (Z_9T), and characterized with X-ray diffraction, SEM and UV–DR spectra. The X-ray diffraction pattern of nanophotocatalyst sample is shown in Fig. 4.23. The average crystallite size of sample was calculated to be about 21.48 nm using the Debye-Scherrer equation and the calculated band gap was found to be 3.60. The

structure and morphology of the photocatalyst was studied using SEM. Fig. 4.24 show the SEM image of the Z_9T.

The photocatalytic activity of the synthesized heterostructured nanophotocatalyst (Z_9T) was studied using 4-CG, as the model organic compound in the presence of UV light. In order to compare the photocatalytic efficiency of different catalysts, identical experiments were carried out with TiO_2 Degussa, Z_9T and ZnO (Merck) for degradation of 4-CG. Fig. 4.25 shows that the coupled oxide Z_9T has higher photocatalytic efficiency of 98.06% than 92.7% which was obtained with ZnO (M) at pH 10. Z_9T also has significantly higher photocatalytic efficiency than Degussa P25 TiO_2 at pH 10. The coupled nanophotocatalyst (Z_9T) was therefore found to be effective in degradation of 4-CG. The order of photocatalytic activity for 4-CG was found to be Z_9T > ZnO(M) > TiO_2 Degussa at pH 10.

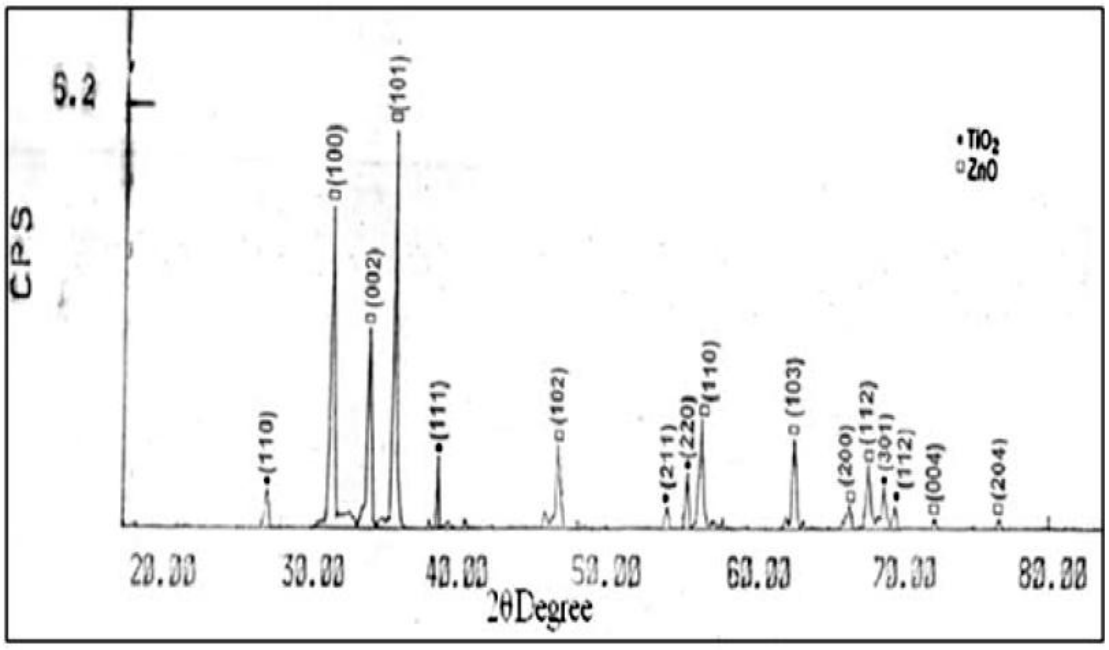


Figure 4.23: XRD pattern of Z_9T

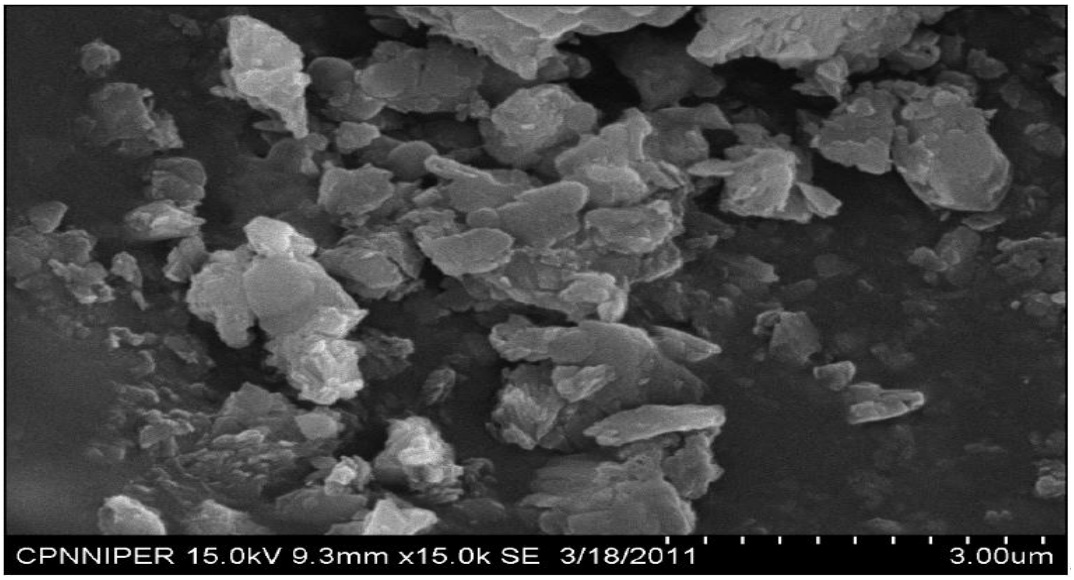


Figure 4.24: SEM surface morphology of heterostructured Z_9T nanophotocatalyst (1 bar length = 300nm)

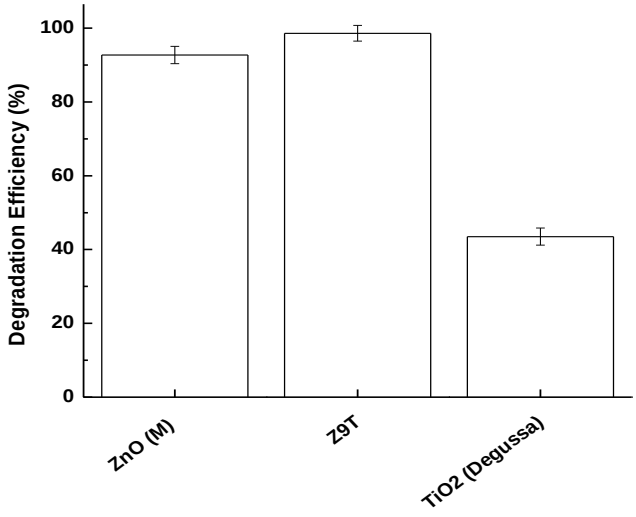


Fig. 4.25: Comparison of degradation efficacy of 4-CG by various photocatalysts (4-CG: 25 mg/L; Catalyst Dose: 2g/L; pH 10; Irradiation time: 6 h)

4.6 COUPLED BIOLOGICAL AND PHOTOCATALYTIC TREATMENT OF BLEACH MILL EFFLUENTS (BME)

The present section describes the studies aimed at employing integrated (biological and photocatalytic) processes for the treatment of chlorination (C) and alkali extraction stage (E_1) effluents from bleaching section of an agro-residue based pulp and paper mill. The photocatalytic degradation using TiO_2 or ZnO in the

presence of sodium hypochlorite (NaOCl) as an oxidant was investigated. In an effort to reduce operational cost, the studies were diverted towards the utilization of solar radiation in the presence of ZnO. This study focused on coupling of photocatalytic treatment with biological process in two different ways viz. photocatalysis prior to biological (Photo+Bio) treatment or photocatalysis followed by biological (Bio+Photo) treatment.

4.6.1 Biological treatment of C and E_1 effluents

The experimental results shown in Fig. 4.26 reveals that after 24 h of biological treatment, the maximum COD removal was found to be 30% for C and 57% for E effluent and no further significant changes were found in the next 5 days. Hence, photocatalytic experiments of biotreated effluents were carried out after 24 h of biological treatment.

4.6.2 Photocatalytic treatment of effluents

The bleach mill effluents from C and E_1 stages were subjected to photocatalytic treatment in the presence of TiO_2 or ZnO as photocatalyst. The effect of variation of pH and presence of NaOCl as an oxidant was also assessed. The initial pH of C and E_1 effluent was observed to be 1.9 and 8.2, respectively.

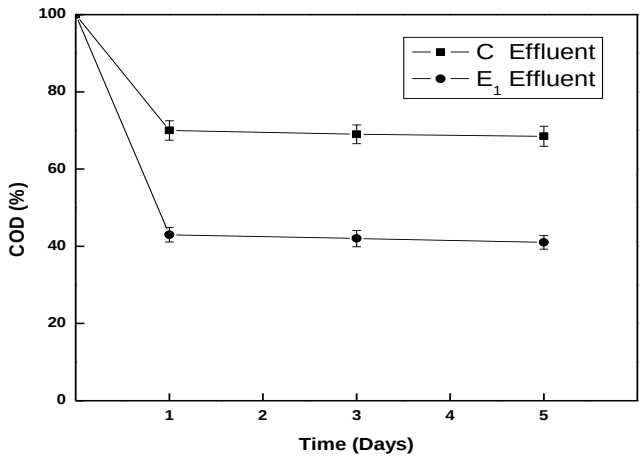


Fig. 4.26 Biological treatment of C and E_1 stage Effluents

4.6.2.1 TiO_2 mediated phototreatment of C effluent

The effluent from chlorination (C) stage was subjected to treatment under different experimental conditions viz UV light alone, UV/NaOCl, Dark+TiO_2 and UV+TiO_2. Fig. 4.27 depicts that there was negligible degradation (4.6%) in the absence of photocatalyst (Only UV). Similarly, in the absence of light (dark/TiO_2 system), the degradation efficiency was 12%. The degradation efficiency of UV/NaOCl system was also observably insignificant (14.5%). Comparatively, UV+TiO_2 system was comparatively effective in the degradation of effluent wherein 42.6% degradability was achieved in 6 h.

In order to further optimize the process parameters i.e. dose of catalyst pH and oxidant concentration, the photocatalytic experiments were performed by varying TiO_2 dose (1 - 4 g/L), pH of the effluent (2-10) and NaOCl concentration (0.005-0.015 M). The graph plotted between amount of catalyst used and the degradation efficiency reveals that maximum degradation of 40.3% was achieved with 3 g/L at original pH of 1.9 as shown in Fig. 4.28(a). The degradation efficiency as a function of pH is shown in Fig. 4.28(b). The results indicate that maximum degradation efficiency of 42.6% was obtained at pH 6.0 with TiO_2 (3 g/L) which was chosen as optimum pH. No changes were observed in pH during the course of degradation. After optimizing the catalyst dose and pH, the effect of oxidant (NaOCl) concentration on the photodegradation efficiency was analyzed. Experiments were conducted by varying the concentration of oxidant from 0.005 to 0.015 M with 3 g/L TiO_2 at pH 6.0. The COD reduction of 47.2% was achieved with 0.01 M concentration of oxidant after 6 h of irradiation (Fig. 4.28(c)). The solar induced photocatalytic treatment was employed for the degradation of C effluent under optimized conditions (TiO_2 3 g/L, pH 6.0, NaOCl 0.01 M) which resulted in

degradation of 45.9% (Fig. 4.28(d)) as compared to 47.2% degradation that occurred in the presence of UV irradiation under similar conditions.

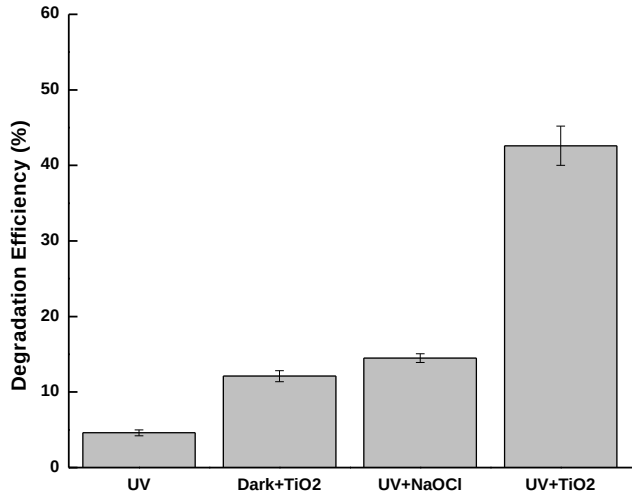


Fig. 4.27: Comparative photolytic and photocatalytic degradation of C effluent (TiO_2 dose: 3 g/L; pH 6.0; NaOCl 0.01 M; Irradiation time: 6 h)

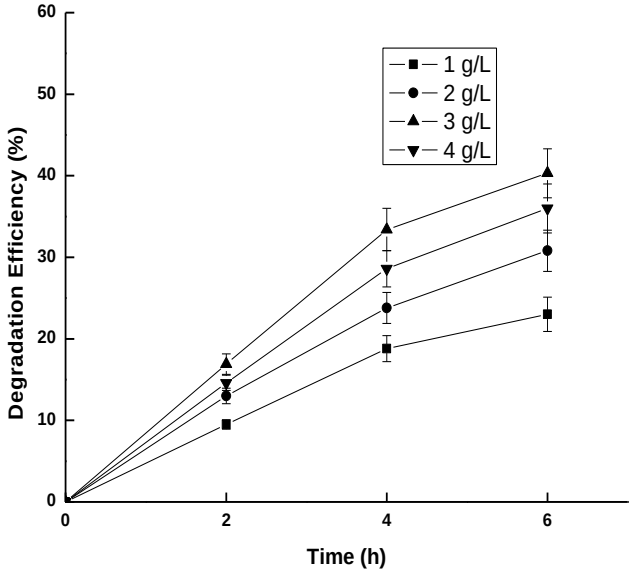


Fig. 4.28(a): Effect of TiO_2 dose on the degradation of C effluent (pH 1.9; Irradiation time: 6 h)

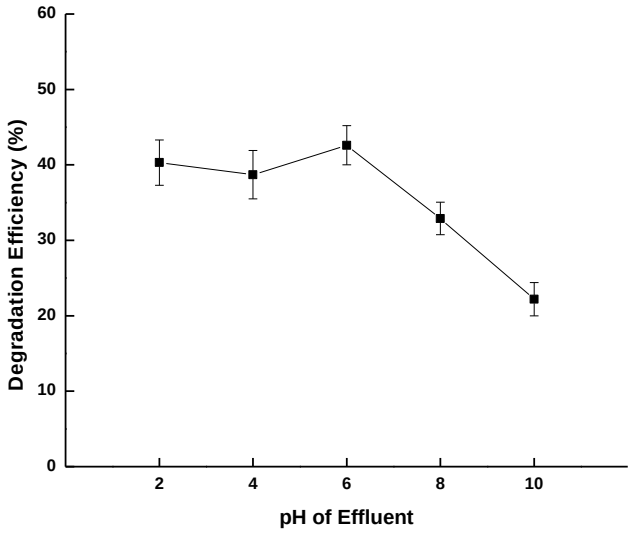


Fig. 4.28(b): Effect of pH on the degradation of C effluent (TiO_2 dose: 3 g/L; Irradiation time: 6 h)

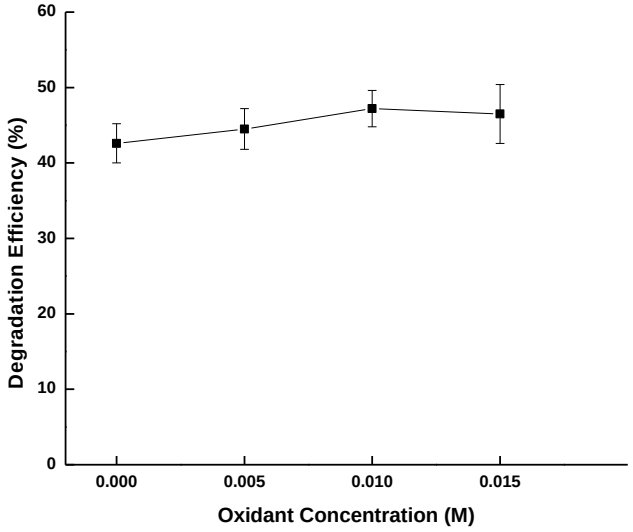


Fig. 4.28(c): Effect of NaOCl concentration on the degradation of C effluent (TiO_2 dose: 3 g/L; pH 6.0; Irradiation time: 6 h)

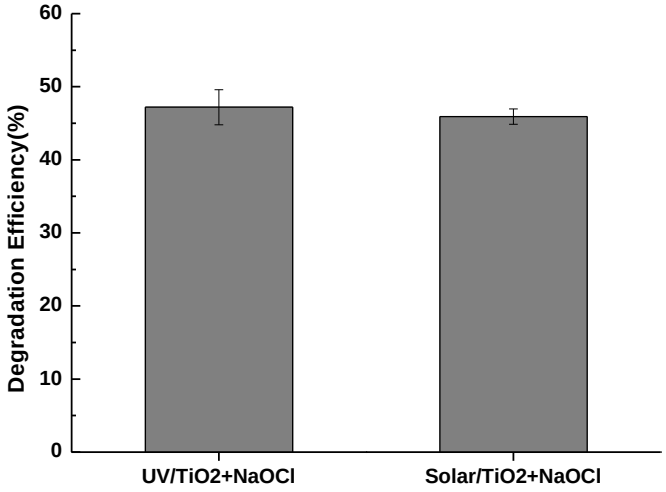


Fig. 4.28(d): Effect of UV/solar light on the degradation of C effluent (TiO_2 dose: 3 g/L; pH 6.0; NaOCl: 0.01 M; Irradiation time: 6 h)

4.6.2.2 TiO_2 mediated phototreatment of E_1 effluent

Figure 4.29 shows the degradation efficiency versus irradiation time for degradation of alkali extraction stage (E_1) effluent in different systems: in the dark or under UV light; in presence or absence of NaOCl/photocatalyst; and combinations of these systems (UV, UV/NaOCl, dark/TiO_2 and UV/TiO_2). Direct photolysis has not been found to be effective in the degradation of effluent as observed with C effluent. In the presence of UV/NaOCl, an insignificant (8.5%) degradation of effluent was observed. In the absence of light (dark/TiO_2 system), less degradation efficiency of 6% has been observed. However, the UV/TiO_2 system facilitated degradation of effluent to an extent of 26%.

The parametric optimization of E_1 effluent was performed in order to assess the effect of catalyst loading, the experiments were performed by varying the catalyst dose (TiO_2) from 1 - 3 g/L at pH (8.2) and irradiation time of 6 h as shown in Fig. 4.30(a). The degradation efficiency increased to 22% when increasing the TiO_2 loading up to 2.5 g/L. However, further increase in catalyst loading (> 2.5 g/L) did not lead to higher degradation efficiency. The role of pH on the rate of photocatalytic

degradation of E_1 effluent was studied in the pH range of 2-10. Fig. 4.30(b) shows that the maximum degradation efficiency of 26% could be achieved with TiO_2 (2.5 g/L) at pH of 4.0. Addition of sodium hypochlorite as an oxidant along with TiO_2 (2.5 g/L) enhanced the rate of photocatalytic degradation of effluent. Fig. 4.30(c) shows that by adding oxidant in the concentration range of 0.01 M to 0.04 M, the rate constant enhanced with increase in concentration of oxidant and maximum degradation efficiency of 37% was observed with 0.03 M NaOCl concentration after 6 h of UV irradiation. In order to check the efficacy of degradation in the presence of solar light, the experiment was conducted under optimized conditions (TiO_2 dose 2.5 g/L; pH 4.0; NaOCl: 0.03 M). Fig. 4.30(d) showed that the degradation achieved in solar light was 35.2% which is relatively closer to the degradation observed in UV light (37%).

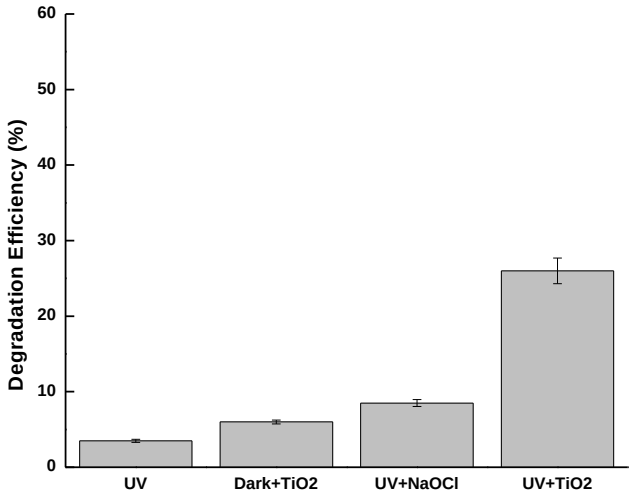


Fig. 4.29: Photolysis and photocatalysis for degradation of E_1 effluent (TiO_2 dose 2.5 g/L; pH 4.0; NaOCl: 0.03 M)

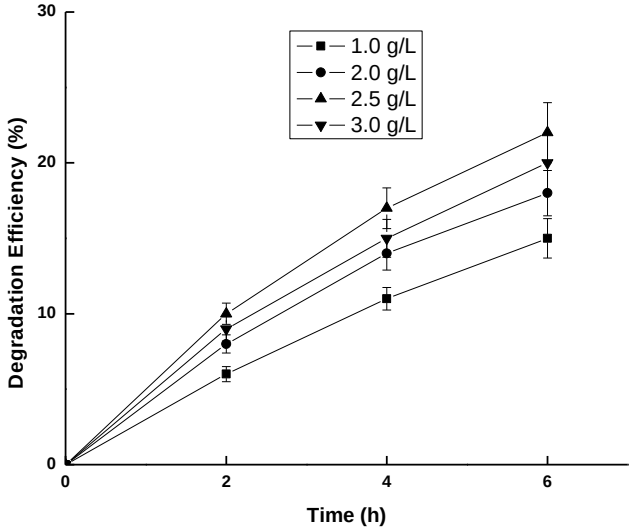


Fig. 4.30(a): Effect of TiO_2 dose on the degradation of E_1 effluent (pH 8.2; Irradiation time: 6 h)

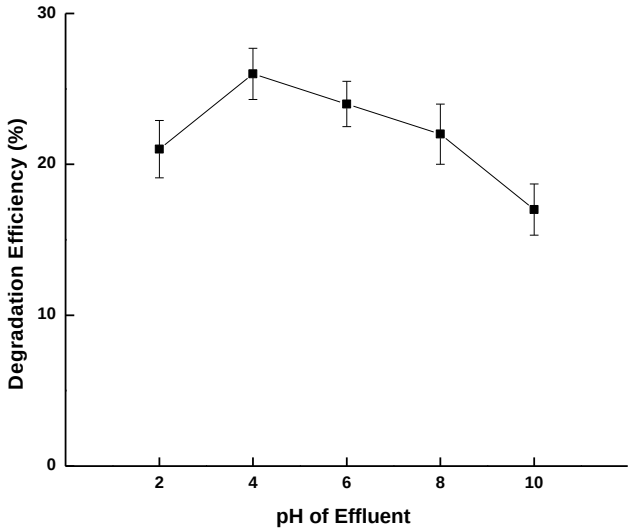


Fig. 4.30(b): Effect of pH on the degradation of E_1 effluent (TiO_2 dose 2.5 g/L; Irradiation time: 6 h)

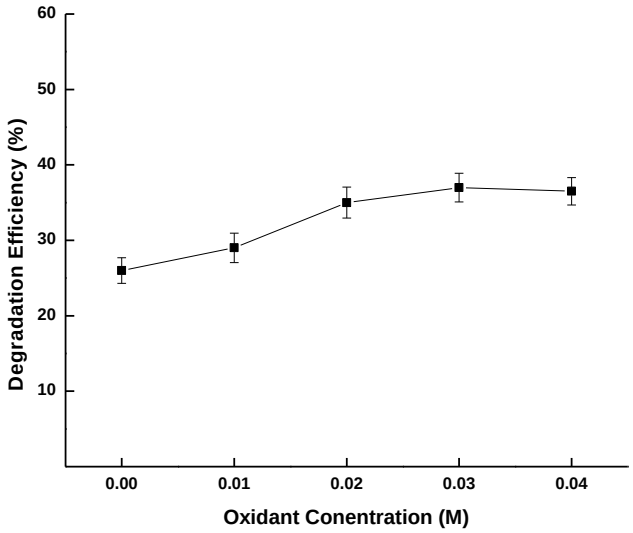


Fig. 4.30(c): Effect of NaOCl concentration on the degradation of E_1 effluent (TiO_2 dose 2.5 g/L; pH 4.0; Irradiation time: 6 h)

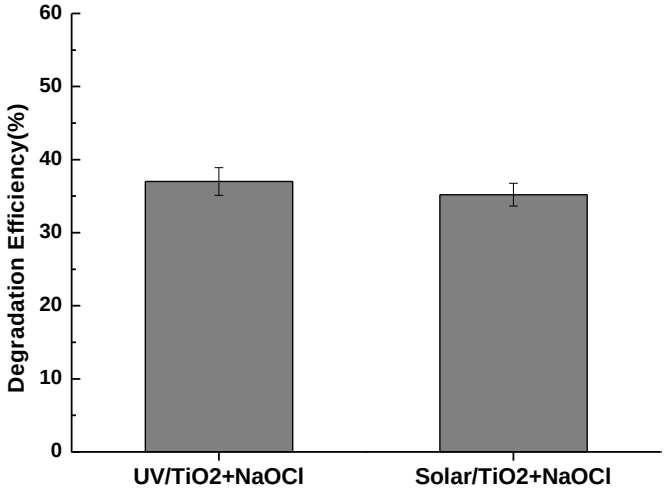


Fig. 4.30(d); Effect of UV/solar light on the degradation of E_1 effluent (TiO_2 dose 2.5 g/L; pH 4.0; NaOCl: 0.03 M; Irradiation time: 6 h)

4.6.2.3 ZnO mediated phototreatment of C effluent

Similarly, the photocatalytic experiments were carried out by varying ZnO dose (1 - 3 g/L) and pH of the effluent (2-12) and concentration of oxidant (NaOCl) from 0.005 to 0.015 M in the presence of UV irradiation. Fig. 4.31(a) shows the effect of variation of catalyst dose used upon the degradation efficiency. The extent of degradation increased upto 46.4% with 2.5 g/L of catalyst dose. However,

further increase of dose beyond 2.5 g/L, reduced degradation to 44.9% with 3.0 g/L ZnO dose. It is evident from the graph that the rate of degradation was higher in the initial phase (first 2 h) of exposure. The effect of pH on degradation efficiency is shown in Fig. 4.31(b). The results reveal that after 6 h of UV irradiation, the maximum degradation efficiency of 54.5% was obtained at pH 8.0 with 2.5 g/L ZnO which was chosen as an optimum pH for subsequent experimentation. Further, photocatalytic experiments were conducted by varying the concentration of oxidant (NaOCl) from 0.005 to 0.015 M with 2.5 g/L ZnO at pH 8.0 under UV irradiation and results are depicted in Fig. 4.31(c). The presence of oxidant did not result in any increase in degradation efficiency of C effluent and rather a decrease in degradation efficiency was observed at higher doses of NaOCl. Fig. 4.31(d) shows that the degradation efficiency in both UV and solar mode under optimized conditions (ZnO 2.5 g/L, pH 8) and degradation in solar irradiation was found to be 53.1% which was similar to that attained in the UV light (54.5%) after 6 h of exposure, with no statistically significant difference. Moreover, the pH at the end of the experiment was found to be 7.5-8.0.

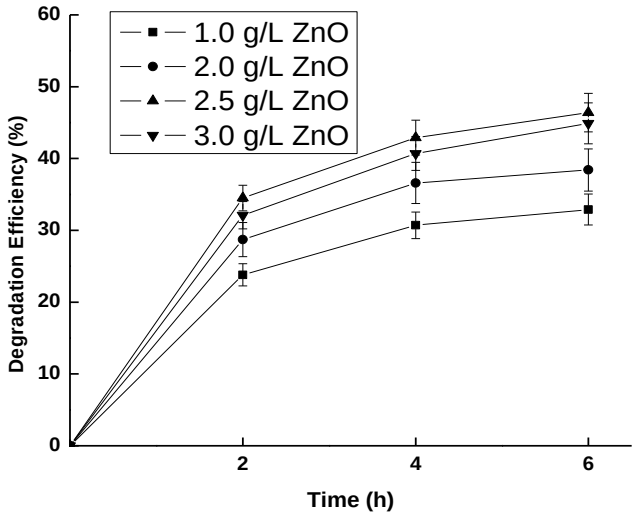


Fig. 4.31(a): Effect of ZnO dose on the degradation of C effluent (pH 1.9; Irradiation time: 6 h)

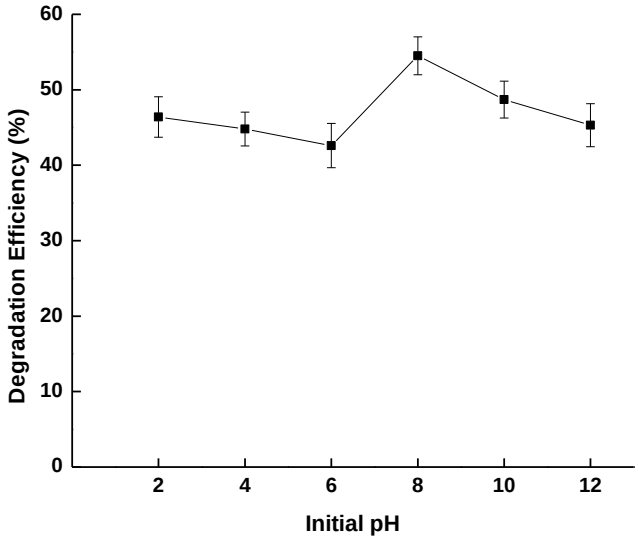


Fig. 4.31(b): Effect of pH on the degradation of C effluent (ZnO dose: 2.5 g/L; Irradiation time: 6 h)

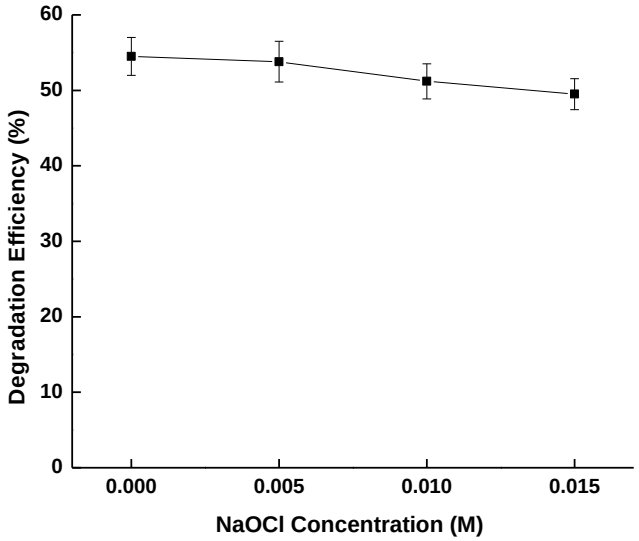


Fig. 4.31(c): Effect of NaOCl concentration on the degradation of C effluent (ZnO dose: 2.5 g/L; pH 8.0; Irradiation time: 6 h)

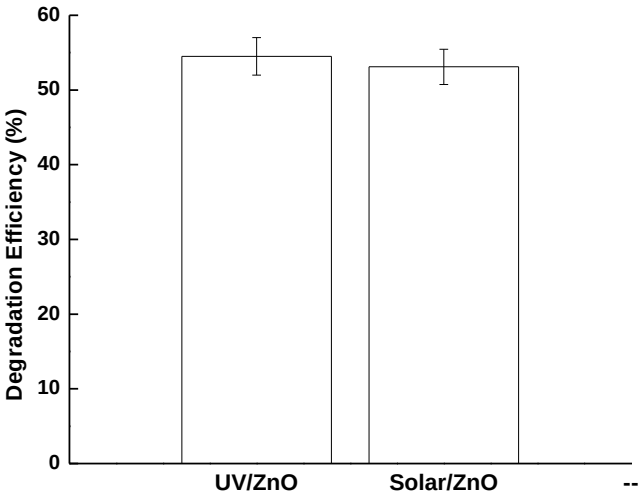


Fig. 4.31(d): Effect of UV/solar light on the degradation of C effluent (ZnO dose : 2.5 g/L; pH 8.0; Irradiation time: 6 h)

4.6.2.4 ZnO mediated phototreatment of E_1 effluent

E_1 effluent was subjected to UV photocatalytic treatment under different conditions of catalyst dose from 1 - 3 g/L, pH in the range of 2-12 and sodium hypochlorite as an oxidant in the concentration range of 0.005 to 0.015 M for the optimization of the process parameters. Fig. 4.32(a) shows degradation efficiency as a function of ZnO dose at original pH (8.2) for the reaction time of 6 h. The degradation efficiency increased to 44.5% when increasing the ZnO loading up to 2.5 g/L. Further, increasing the catalyst loading (> 2.5 g/L) resulted in lower degradation efficiency of 42.2 % with 3.0 g/L ZnO. Fig. 4.32(b) depicts that the maximum degradation efficiency of 44.5% was achieved with ZnO (2.5 g/L) at pH 8.0. Addition of oxidant (NaOCl) in the concentration range of 0.005 to 0.015 M along with 2.5 g/L ZnO at pH 8 (Fig. 4.32(c)) did not improve the degradation efficiency of effluent. The effect of UV/solar irradiation on the degradation efficiency under optimized conditions (2.5 g/L ZnO, pH 8) is shown in Fig. 4.32(d) and degradation efficiency in solar mode

(43%) was relatively closer to that observed under UV irradiation (44.5%) after 6 h of exposure.

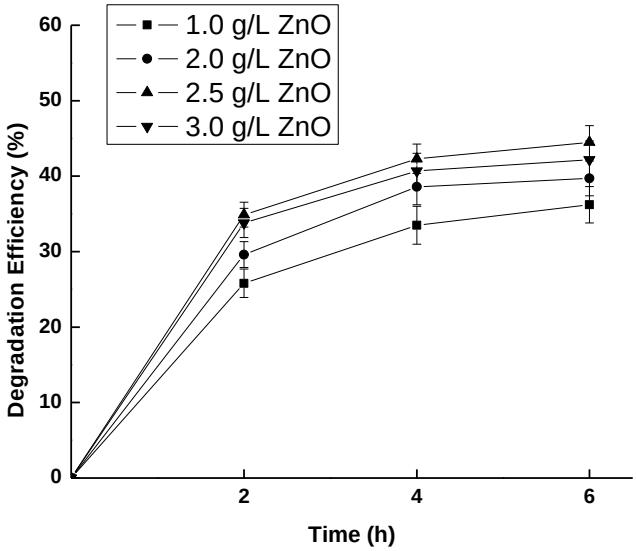


Fig. 4.32(a): Effect of ZnO dose on the degradation of E_1 effluent (pH 8.2; Irradiation time: 6 h)

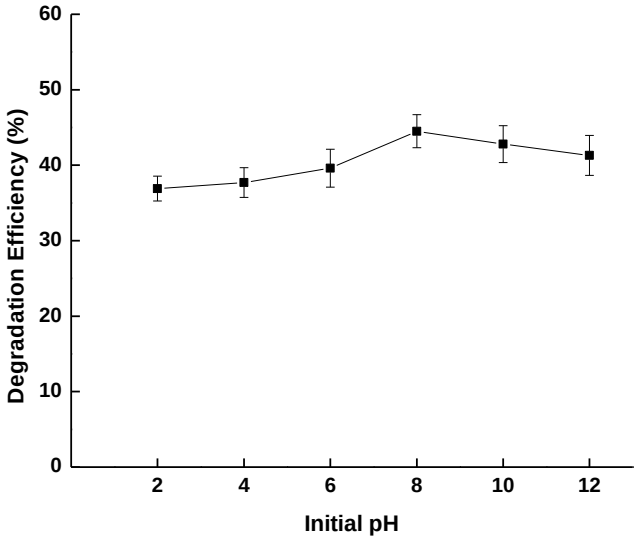


Fig. 4.32(b): Effect of pH on the degradation of E_1 effluent (ZnO dose: 2.5 g/L; Irradiation time: 6 h)

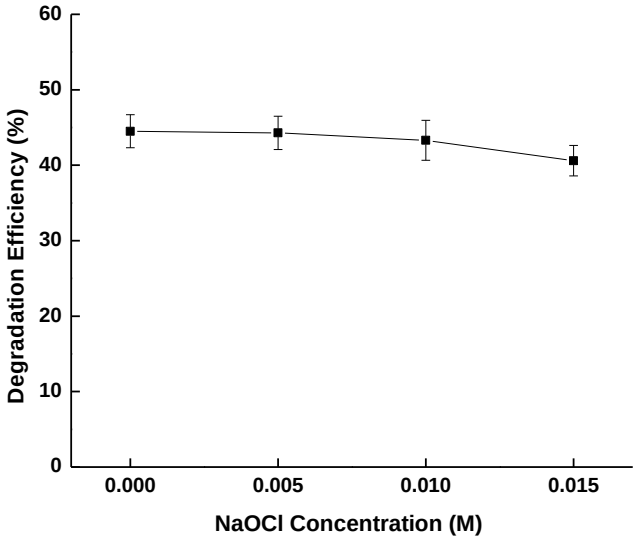


Fig. 4.32(c): Effect of NaOCl concentration on the degradation of E_1 effluent (ZnO dose: 2.5 g/L; pH 8.0; Irradiation time: 6 h)

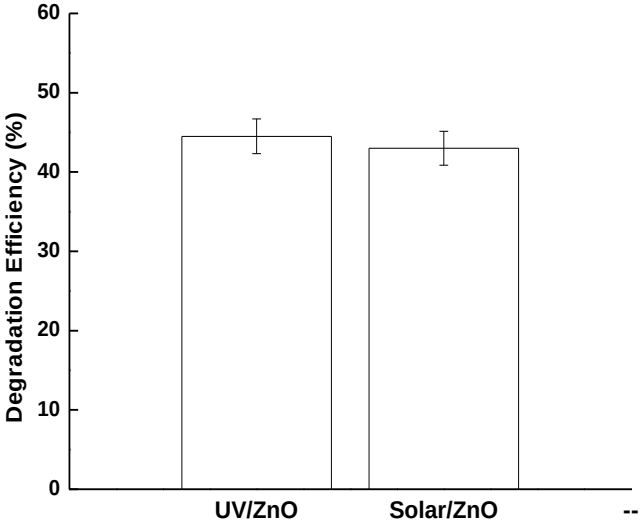


Fig. 4.32(d): Effect of UV/Solar light on the degradation of E_1 effluent (ZnO dose: 2.5 g/L; pH 8.0; Irradiation time: 6 h)

4.6.3 Coupled treatment of effluents

In the coupled treatment of C and E_1 effluents, TiO_2 mediated photocatalytic treatment was carried out in the presence of oxidant (NaOCl) and UV light under optimized conditions (TiO_2 3 g/L, pH 6.0, NaOCl 0.01 M) and (TiO_2 dose: 2.5 g/L; pH 4.0; NaOCl: 0.03 M), respectively however, ZnO mediated photocatalytic

treatment of C and E_1 effluents was performed without oxidant (NaOCl) in solar light under optimized conditions (ZnO dose 2.5 g/L, pH 8.0) and (ZnO dose 2.5 g/L; pH 8.0), respectively.. The degradation efficiency was measured in terms of COD reduction.

. **4.6.3.1 Coupled treatment of C effluent**

The sequential process involving biological-photocatalytic treatment (Bio+Photo) and the reverse sequential treatment (Photo+Bio) were applied to C effluents. The sequential biological (24 h) – UV/TiO_2/NaOCl (2 h) resulted in 81.5% degradation under optimized conditions (Fig. 4.33(a)). In contrast, only 30% and 47% degradation efficiency could be achieved for C effluent with independent biological and photocatalytic treatment (UV/TiO_2/NaOCl), respectively. A degradation of 89.6% degradation was achieved with sequential UV/TiO_2/NaOCl (2 h) – biological (24 h) system. Fig. 4.33(b) shows the degradation efficiency of the treatment of C effluent by independent biological, photocatalytic (ZnO) as well as the coupled processes. The sequential biological (24 h) – solar/ZnO (2 h) resulted in 85.5% degradation which was significantly different when compared to biological (Bio) treatment alone (30%). The degradation of 92.8% was achieved by employing sequential solar/ZnO (1 h) - biological process (24 h) as compared to only 53.1% degradation that occurred in photocatalytic treatment alone (Solar/ZnO) under optimized conditions even after 6 h of irradiation. Fig. 4.34 shows the changes in biodegradability with solar/ZnO as a function of irradiation time and depicts that biodegradability increased from 0.34 to 0.65 after 1 h of treatment. Employing 1 h of photocatalytic (solar/ZnO) treatment followed by 12 h and 24 h biological treatment resulted in 91.6 and 92.8% degradation, respectively. Hence sequential solar/ZnO (1 h) – biological treatment (12 h) was found to be most efficient in the degradation of C effluent.

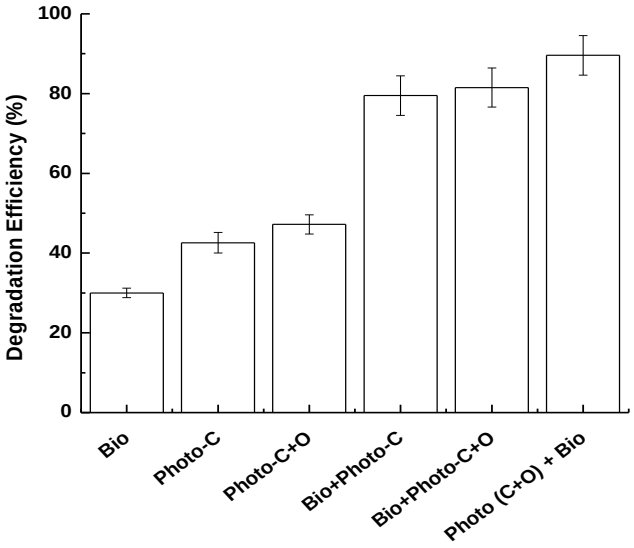


Figure 4.33(a): Degradation of C effluent by independent and coupled treatment
(Bio implies Biological Treatment for 1 day, Photo-C denotes photocatalytic Treatment with TiO_2 and Photo-C+O denotes Photocatalytic Treatment with TiO_2+NaOCl)

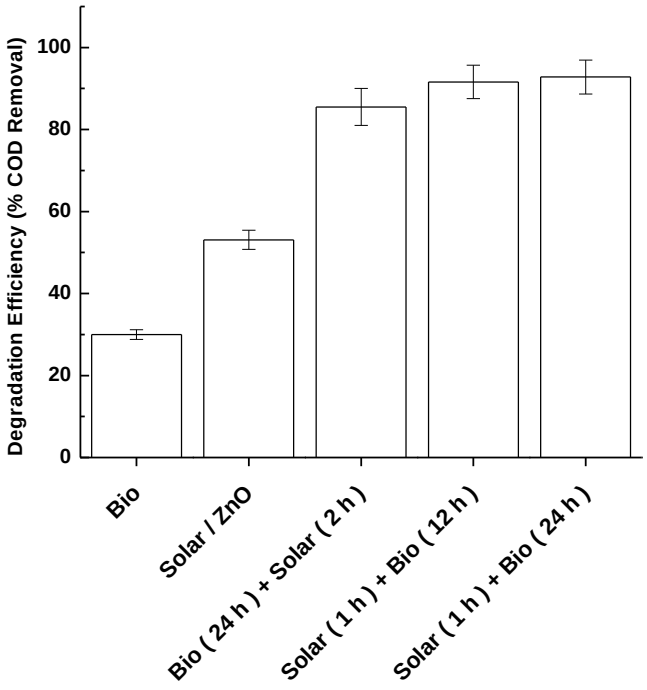


Fig. 4.33(b): Degradation of C effluent by independent and coupled treatment
(Bio implies biological treatment, Solar denotes solar light induced photocatalysis with ZnO)

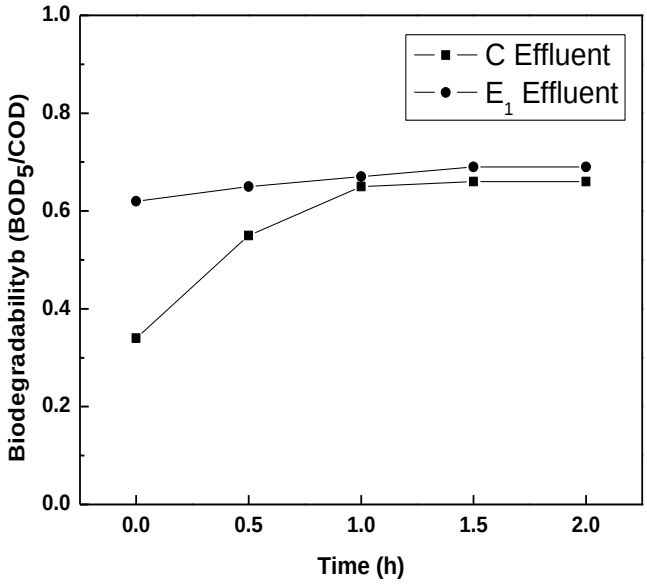


Fig. 4.34: Biodegradability enhancement of C and E_1 effluent (Solar/ZnO)

4.6.3.2 Coupled treatment of E_1 effluent

The sequential biological – photocatalytic (Bio+Photo) and photocatalytic-biological (Photo+Bio) processes were employed for the degradation of E_1 effluent. Biodegradation of 57% was achieved after 24 h of biological treatment (Bio) alone due to better biodegradability of E_1 as compared to C effluent. Fig. 4.35(a) shows maximum degradation of 93% for E_1 effluent with sequential biological (24 h) – UV/TiO_2/NaOCl (2 h) as compared to 87.3% degradation which occurred with sequential UV/TiO_2/NaOCl (2 h) - biological treatment (24 h). Fig. 4.35(b) shows that sequential biological (24 h) – solar/ZnO (2 h) resulted in 95.4% degradation as compared to 84.8% degradation which occurred with sequential solar/ZnO (2 h) - biological (24 h) treatment. In contrast, about 37 and 43% degradation efficiency was attained with UV/TiO_2/NaOCl and Solar/ZnO treatment under optimized conditions of catalyst dose and pH even after 6 h of irradiation.

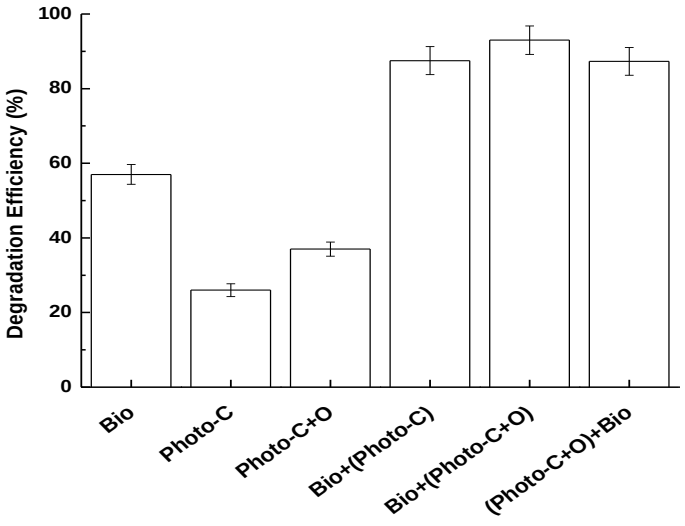


Figure 4.35(a): Degradation of E_1 effluent by independent and coupled treatment
(Bio implies Biological Treatment for 1 day, Photo-C denotes photocatalytic Treatment with TiO_2 and Photo-C+O denotes Photocatalytic Treatment with TiO_2+NaOCl)

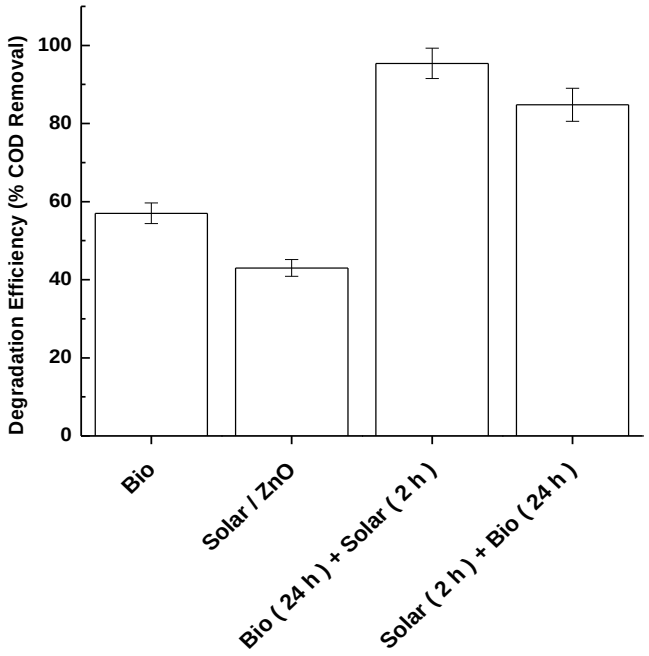


Fig. 4.35(b): Degradation of E_1 effluent by independent and coupled treatment
(Bio implies biological treatment, Solar denotes solar light induced photocatalysis with ZnO)

4.6.4 TOC abatement studies

As the reduction of TOC reflects the extent of mineralization of various organic species present in the effluents, the percentage reduction in TOC was studied for both effluents with different treatment processes. In the coupled treatment of C

and E_1 effluents, photocatalytic treatment was carried out with 3.0 g/L TiO_2, pH 6.0, 0.01 M NaOCl and 2.5 g/L TiO_2, pH 4.0, 0.03 M NaOCl, respectively. In case of ZnO, photocatalytic treatment of C and E_1 effluents was performed in solar light under optimized conditions (2.5 g/L ZnO, pH 8.0) and (2.5 g/L ZnO, pH 8.0), respectively. Figures 4.36(a) and 4.36(b) indicates that TOC value decreases with the degradation of organic compounds present in the effluents. The initial TOC value of C stage effluent was 400 mg/L which decreased to 315 and 240 mg/L with independent biological and TiO_2 mediated photocatalytic treatment (under optimized conditions) respectively. The coupled photocatalytic-biological treatment of C effluent resulted in TOC of 68 mg/L however; the coupled biological-photocatalytic treatment resulted in TOC of 82 mg/L. Similarly for E_1 effluent, the initial TOC (560 mg/L) was reduced to 74 and 60 mg/L with sequential photocatalytic-biological and biological-photocatalytic treatment, respectively.

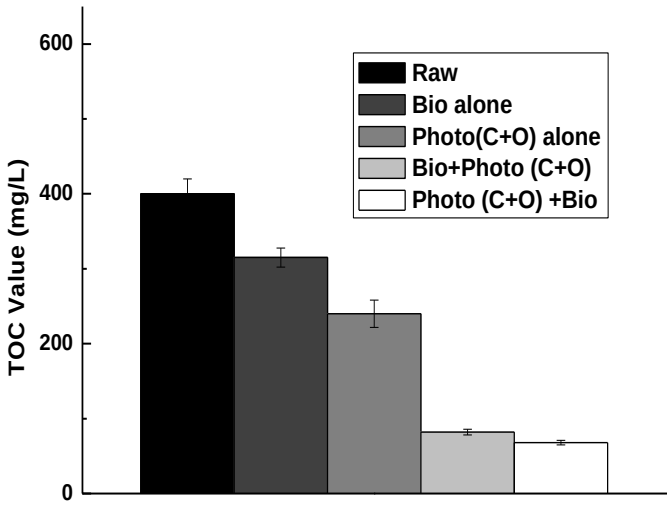


Fig. 4.36(a): TOC removal by independent and coupled treatment of C effluent (TiO_2 dose: 3.0 g/L; pH 6.0; 0.01 M NaOCl)

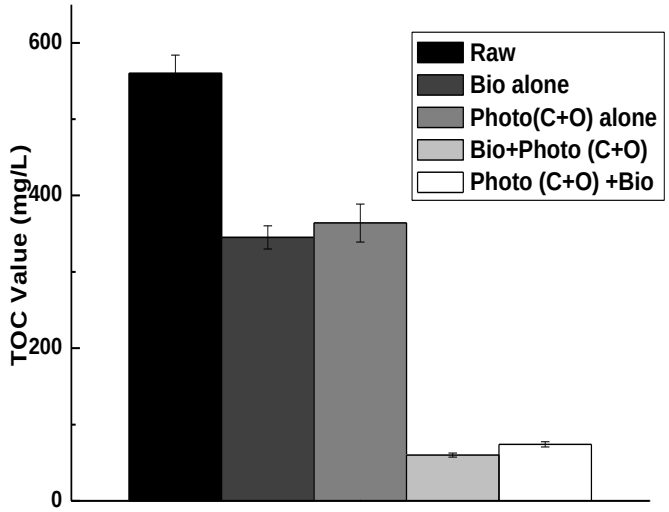


Fig. 4.36(b): TOC removal by independent and coupled treatment of E_1 effluent (TiO_2 dose: 2.5 g/L; pH 4.0; 0.03 M NaOCl)

Figures. 4.37(a) and 4.37(b) shows the reduction in TOC using ZnO mediated photocatalytic treatment coupled with biological treatment. For C effluent, solar assisted AOP using ZnO (1 h) followed by biological treatment (12 h) resulted in higher TOC removal (89%) while, for E_1 effluent, biological treatment (24 h) followed by Solar/ZnO (2 h) system was more efficient as 91% reduction of TOC was achieved.

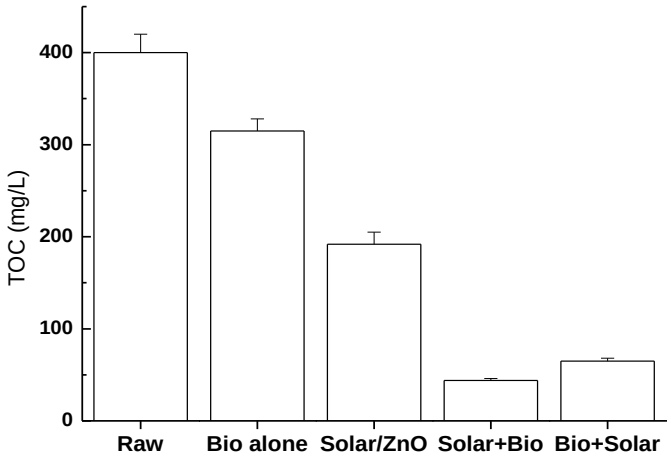


Fig. 4.37(a): TOC removal by independent and coupled treatment of C effluent (ZnO dose: 2.5 g/L; pH 8.0)

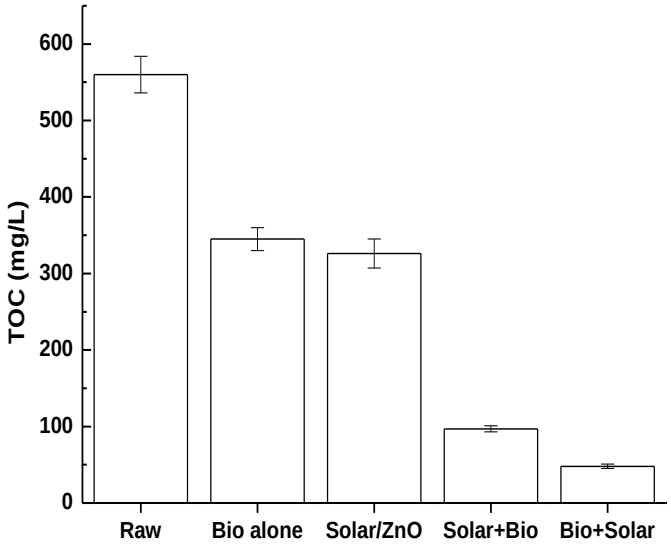


Fig. 4.37(b): TOC removal by independent and coupled treatment of E_1 effluent (ZnO dose: 2.5 g/L; pH 8.0)

4.6.5 GC-MS studies

The C stage bleach mill effluent samples treated with UV/TiO_2 or solar/ZnO photocatalytic system for 6 h under optimized conditions (2.5 g/L TiO_2; pH 6.0; 0.01 M NaOCl and 2.5 g/L ZnO; pH 8) were further subjected to hyphenated GC-MS technique in order to assess the fate of model organic compounds during the photocatalytic process. The GC-MS chromatograms shown in Figs. 4.38(a) and 4.38(b) depict the photocatalytic degradation of the model compounds in the real time bleach mill effluent using TiO_2 and ZnO, respectively. The decreases of characteristic peaks with photocatalysis confirmed the degradation of model compounds in particular and bleach mill effluents in general.

The reduction in quantity of 4-CG and 4-CC (having retention time of 23.67 and 18.70 respectively) in the ZnO and TiO_2 treated samples (Table 4.9) suggests that photocatalysis is effective in the degradation of these compounds even in the bleach mill effluents.

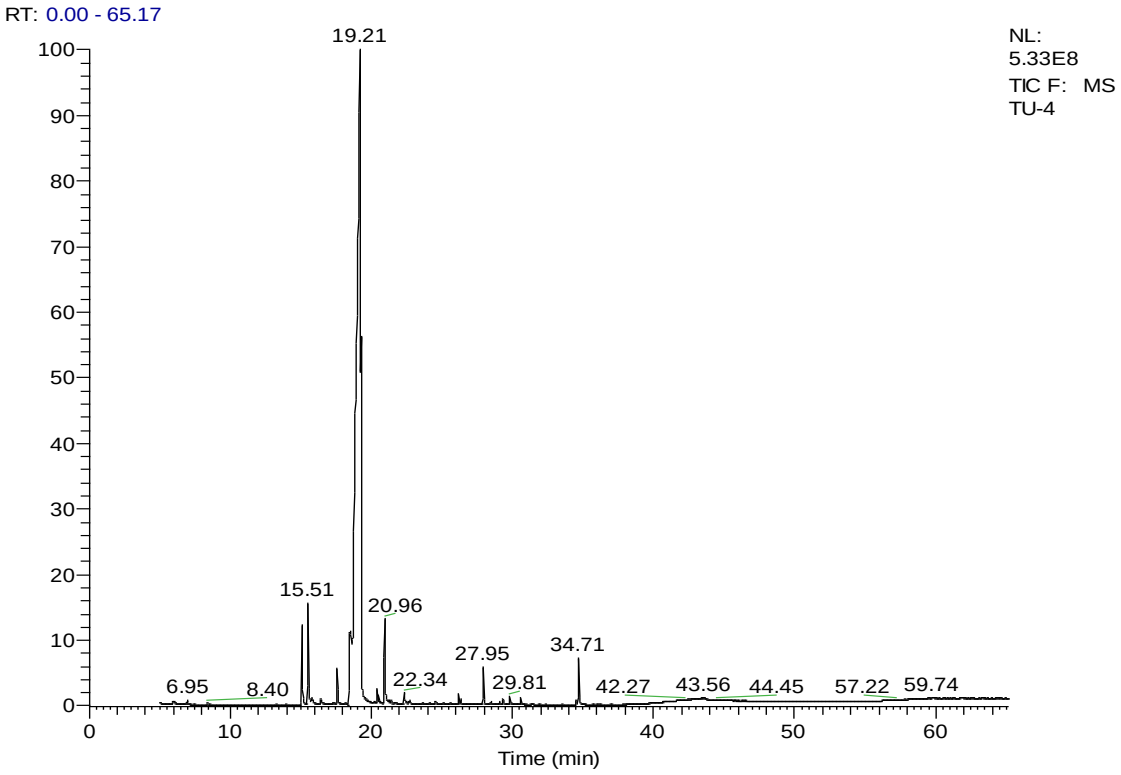


Fig. 4.38(a): GC-MS chromatograms of TiO_2 treated bleach mill effluent

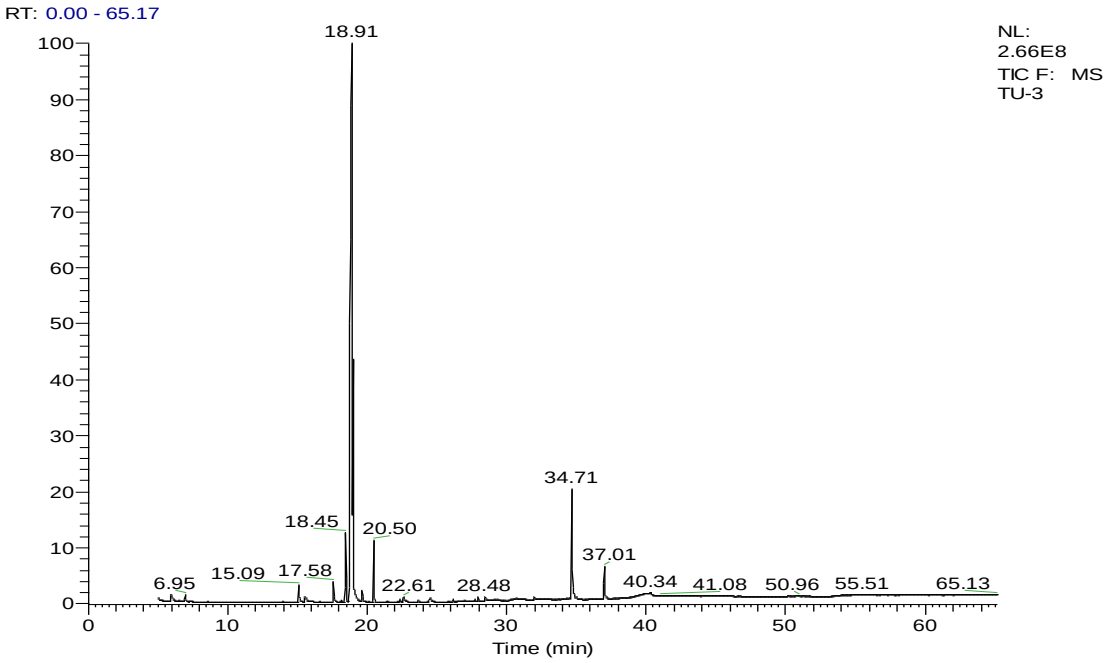


Fig. 4.38(b): GC-MS chromatograms of ZnO treated bleach mill effluent

Table: 4.9. Quantitative analysis of different model compounds using GC-MS

S. N.	Name of compound	RT (min)	Quantity (ug/L)		
			Untreated Effluent	ZnO Treated Effluent	TiO_2 Treated effluent
1	4-chlororcatechol	23.67	1624.47	43.5	78.56
2	4-chloroguaiacol	18.70	2002.4	53.2	112.8

4.7 INTEGRATED PHOTOCATALYTIC AND BIOLOGICAL TREATMENT OF COMBINED PULP AND PAPER MILL EFFLUENTS

Further, the present study evaluated the response of integrated photocatalytic and biological treatment for the degradation of combined pulp and paper mill effluents. The effluent samples were procured from functional ETP (having sequential anaerobic (UASB) followed by two stage activated sludge process) of agro residue based pulp and paper mill. The samples were collected from three different stages of ETP viz. (i) inlet point after primary clarification termed as *Raw* effluent, (ii) after anaerobic treatment termed as *Stage-1* effluent and (iii) after sequential anaerobic – aerobic (I) treatment termed as *Stage-2* effluent. The *stage-1* and *stage-2* effluent samples experienced degradation of approx. 53% and 84% with anaerobic (UASB) and sequential anaerobic-aerobic (UASB-ASP) treatment at industrial ETP. The photocatalytic treatment of all the three effluent samples was carried out with UV as well as solar light using TiO_2/ZnO. The integrated treatment involving photocatalytic (Solar/ZnO) followed by biological treatment was employed to *stage-1* and *stage-2* effluent samples in order to constitute sequential treatments namely anaerobic-photocatalytic-aerobic and anaerobic-aerobic-photocatalytic-aerobic processes, respectively. The degradation efficiency was evaluated in terms of COD reduction. The option of applying photocatalyst in the immobilized mode was also adjudged.

4.7.1 TiO_2 mediated phototreatment of effluents

The response to photocatalysis was assessed for *raw, Stage-1* and *Stage-2* effluent samples at their existing pH. In order to optimize dose of catalyst, the photocatalytic experiments were performed by varying TiO_2 dose (1.0 – 3.0 g/L) for all the effluent samples in the presence of UV irradiation. Fig. 4.39(a) shows that maximum degradation of *raw* effluent obtained was 21.4% at dosage of either 2.0 or 3.0 g/L of TiO_2. In case of samples from *Stage-1* and *Stage-2* the maximum degradation of 35.2 and 23.9% was achieved at 2.5 and 2.0 g/L, respectively (Figs. 4.39(b) & 4.39(c)**)**. In order to check the efficacy of TiO_2 in the presence of different light sources, all the three effluent samples were subjected to treatment under different conditions viz Dark/TiO_2, UV/TiO_2 and Solar/TiO_2. Experiments were conducted with TiO_2 dose of 2.0, 2.5 and 2.0 g/L for degradation of *raw, stage-1* and *stage-2* effluents. Fig. 4.39(d) depicts that there was less degradation (10%) in the absence of light (dark/TiO_2) system. Solar/TiO_2 system was found to be as effective as UV/TiO_2 in the degradation of *raw, Stage-1* and *Stage-2* effluents.

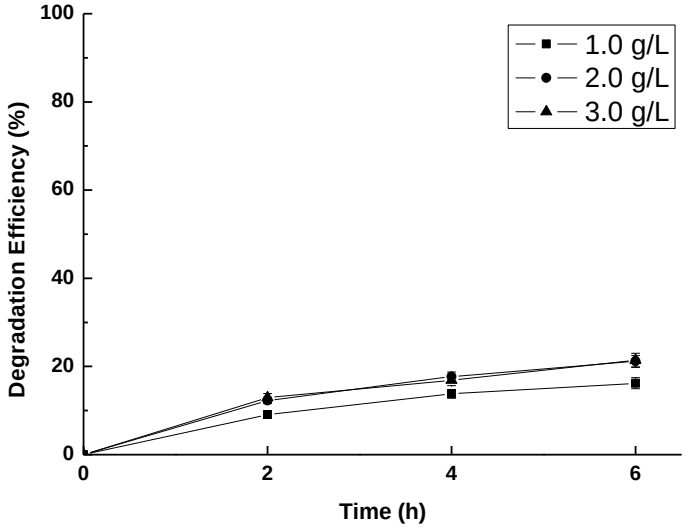


Fig. 4.39(a): Degradation of *Raw* effluent using different dosages of TiO_2

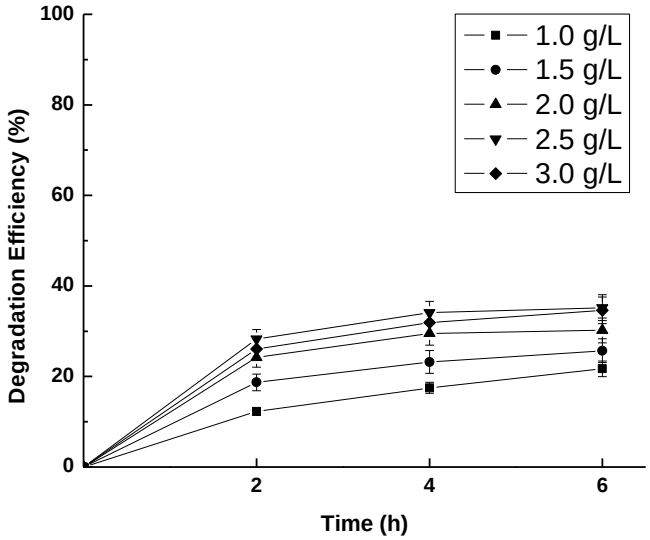


Fig. 4.39(b): Degradation of *Stage-1* effluent using different dosages of TiO_2

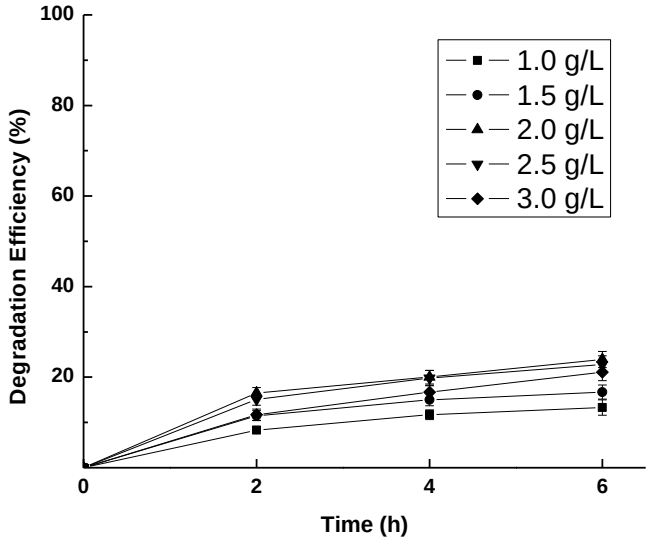


Fig. 4.39(c): Degradation of *Stage-2* effluent using different dosages of TiO_2

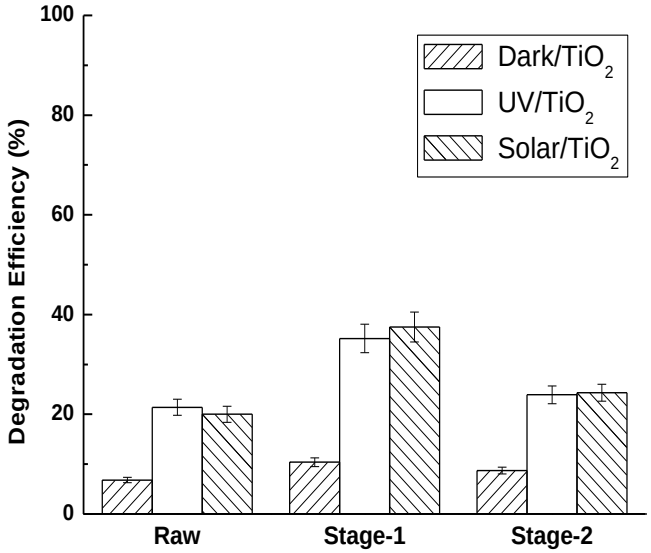


Fig. 4.39(d): Effect of light source on the degradation of effluents (TiO_2 dose: 2.0, 2.5 and 2.0 g/L for *Raw, stage-1* and *stage-2* effluents resp.)

4.7.2 ZnO mediated photocatalysis

The experiments were performed by varying the catalyst dose (ZnO) from 1.0 – 3.0 g/L for *raw, Stage-1* and *Stage-2* effluent samples at natural pH and irradiating in UV for 6 h. The degradation of *raw* effluent was found to be about 26% with 3 g/L of ZnO dose (Fig. 4.40(a)). The degradation efficiency of ZnO was examined for *Stage-1* and *Stage-2* effluent samples by varying the catalyst dose following approach similar to TiO_2 explained earlier. The extent of degradation was 46.4% with 2.0 g/L of ZnO after 6 h of UV irradiation (Fig. 4.40(b)) in case of *Stage-1* and 36.7% in case of *Stage-2* with ZnO dose of 1.5 g/L (Fig. 4.40(c)). Further, increase in catalyst dose resulted in the decrease of degradation efficiency. The effluent samples were also subjected to different degradation systems viz. dark/ZnO, UV/ZnO and Solar/ZnO under optimized dosages of ZnO i.e. 3.0, 2.0 and 1.5 g/L for the degradation of *raw, stage-1* and *stage-2* effluents. In the absence of light (dark/ZnO system), degradation efficiency less than 12% has been observed. The Solar/ZnO system facilitated degradation of effluent to an extent similar to that of UV/ZnO system (Fig. 4.40(d)).

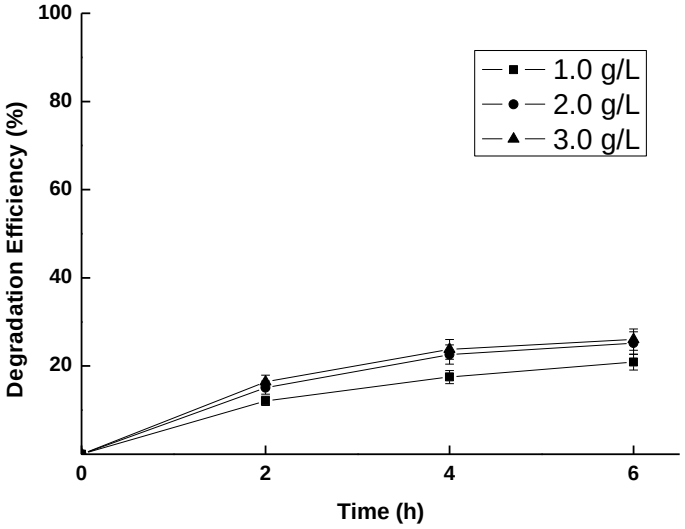


Fig. 4.40(a): Degradation of *Raw* effluent using different dosages of ZnO

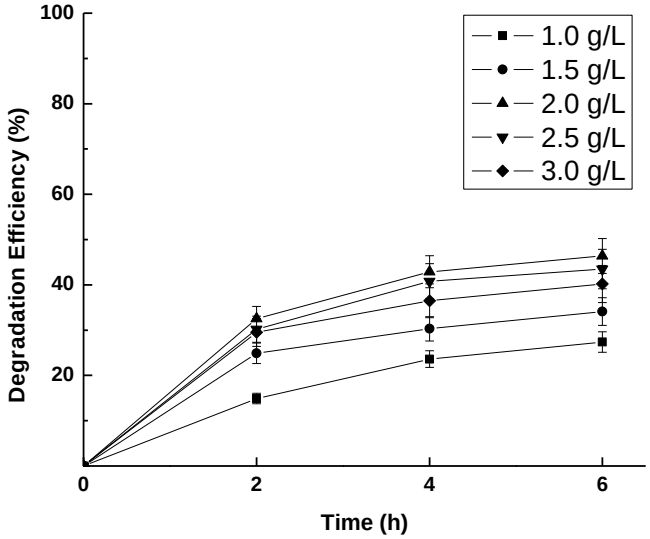


Fig. 4.40(b): Degradation of *Stage-1* effluent using different dosages of ZnO

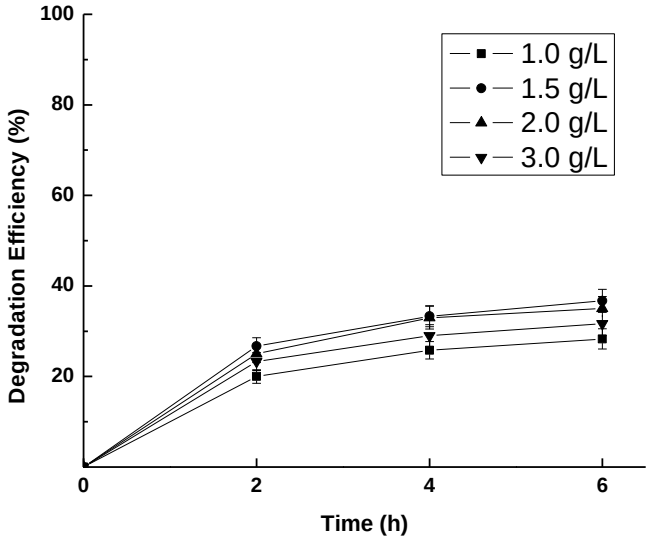


Fig. 4.40(c): Degradation of *Stage-2* effluent using different dosages of ZnO

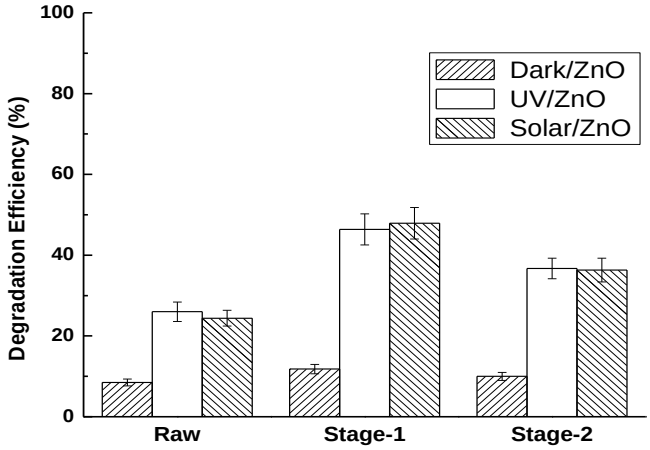


Fig. 4.40(d): Effect of light source on the degradation of effluents (ZnO dose: 3.0, 2.0 and 1.5 g/L for *Raw, stage-1* and *stage-2* effluents resp.)

4.7.3 Sequential photocatalytic-biological treatment of *stage-1* effluent

The *Stage-1* effluent sample (having residual COD of 47%) was subjected to sequential photocatalytic involving TiO_2/ZnO in the presence of solar irradiations followed by aerobic biological treatment to obtain integrated anaerobic-photocatalytic-aerobic treatment sequence. The positioning of analysis of the samples during integrated anaerobic-photocatalytic-aerobic sequence is presented in Fig. 4.41.

Both photocatalytic and biological processes were operated in a batch mode. In order to obtain the best compromise between the shorter photocatalytic and the longer biological treatments as well as better treatment efficacy, the biological treatment was employed after 1 h and 2 h of photocatalytic treatment. The 1 h phototreatment resulted in 61.9 and 63.4 % of degradation with solar/TiO_2 and solar/ZnO systems, respectively (Table 4.10). However, 2 h phototreatment yielded better outcome with the degradation efficiency increased to 66.9 and 68.8 % with solar/TiO_2 and solar/ZnO systems, respectively. The percent degradation(s) mentioned here are with reference to COD content of the *raw* effluent. The variation in biodegradability (in terms of BOD_5/COD ratio) of the phototreated samples were measured as a function of time. The experiments were conducted under optimized dose (2 g/L ZnO) for different time intervals. A 2 h pretreatment time with Solar/ZnO was noted to be necessary for *Stage-1* sample to enhance the biodegradability from 0.38 to 0.56 and to make the phototreated solution biocompatible. After phototreatment, the samples were subjected to batch aerobic treatment for 24 h and the extent of degradation was 87.8 and 89.9% with anaerobic-solar/TiO_2-aerobic and anaerobic-solar/ZnO-aerobic integrated systems, respectively.

4.7.4 Sequential photocatalytic-biological treatment of *stage-2* effluent

As an alternative option, the *Stage-2* effluent samples (having residual COD of 16%) were subjected to sequential photocatalytic-biological treatment so as to obtain integrated anaerobic-aerobic-photocatalytic-aerobic treatment sequence. In order to increase the industrial viability of the photocatalysis, the phototreatment was carried out with TiO_2/ZnO in the presence of solar irradiations under optimized conditions of catalyst dose. The phototreated sample after different time intervals of 0.5, 1.0, 1.5 and 2.0 h were collected and changes in biodegradability was determined. The biodegradability was 0.18 and 0.2 after 1 and 2 h of photocatalytic treatment with

Solar/ZnO system. The 1 and 2 h of photo-treated samples were subsequently subjected to biological treatment for 24 h and the degradation efficiencies were monitored after interval of 12 h. The positioning of analysis of the samples during integrated anaerobic-aerobic-photocatalytic-aerobic sequence is presented in Fig. 4.41.

The results shown in Table 4.10 reveal that the extent of degradation in 1 and 2 h of photocatalytic treatment (Solar/ZnO) followed by 12 h of aerobic treatment was 96.8 and 97.1%. In case of solar/TiO_2, photo (1 h)-biological (12 h) and photo (2 h)-biological (12 h) yielded degradation of 94.7 and 95.0%. The percent degradation(s) mentioned here are with reference to COD content of the *raw* effluent. Thus, 1 h of photo treatment (Solar/ZnO) followed by 12 h of aerobic biological treatment applied to *stage-2* effluent (integrated anaerobic-aerobic-photocatalytic-aerobic) has been found to be optimal for achieving significant degradation of organics in effluents.

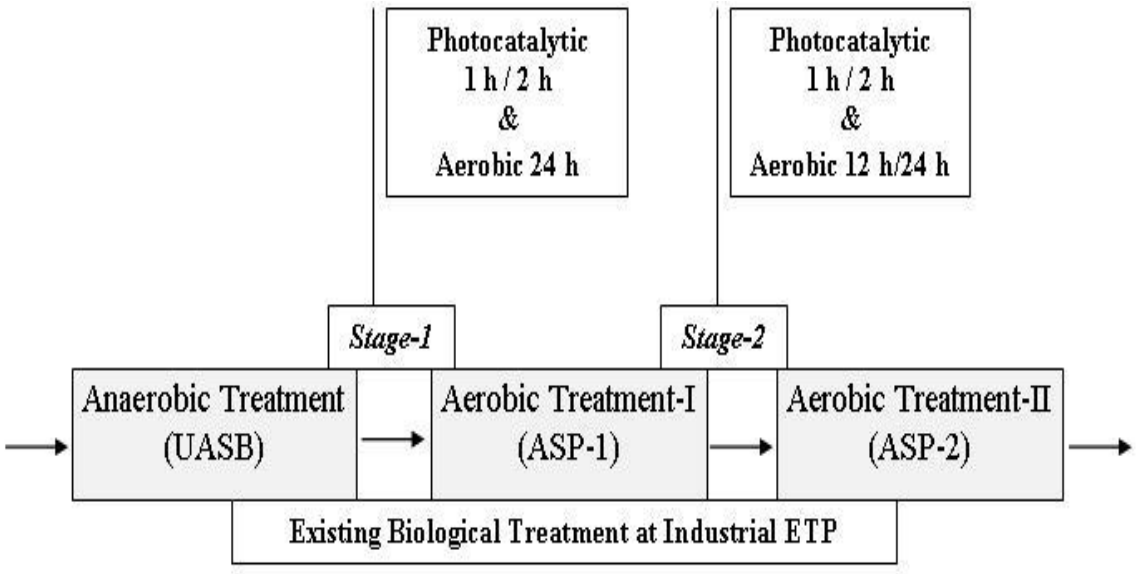


Fig. 4.41: Schematic diagram showing sampling points in integrated treatments

4.7.5 Supported photocatalyst in the phototreatment process

In order to further increase the commercial viability of the coupled system, the photo-treatment step was attempted with immobilized catalyst (ZnO). ZnO was used in the immobilization mode according to the procedure explained in section 3.7.2. Fig. 4.42 shows the comparative evaluation of Solar/ZnO in slurry and in immobilized mode for the photodegradation of *stage-2* effluent. Although the degradation achieved in immobilized mode was less as compared to slurry mode, but supported catalyst system provide an economical approach in use of photocatalysis at industrial level.

Table: 4.10. Comparison of Integrated systems for the degradation efficiencies of pulp and paper mill effluents

S.N.	Type of Sample	Type of Treatment	Degradation Efficiency (%) with Solar/ZnO	Degradation Efficiency (%) with Solar/TiO_2
1.	Stage 1 Effluent Sample	AOP (1 h)	63.4	61.9
		AOP (1 h) + Aerobic (24 h)	86.4	84.4
		AOP (2 h)	68.8	66.9
		AOP (2 h) + Aerobic (24 h)	89.9	87.8
2.	Stage 2 Effluent Sample	AOP (1 h)	86.0	85.5
		AOP (1 h) + Aerobic (12 h)	96.8	94.7
		AOP (1 h) + Aerobic (24)	97.4	95.5
		AOP (2 h)	88.1	87.3
		AOP (2 h) + Aerobic (12 h)	97.1	95.0
		AOP (2 h) + Aerobic (24 h)	97.4	95.8

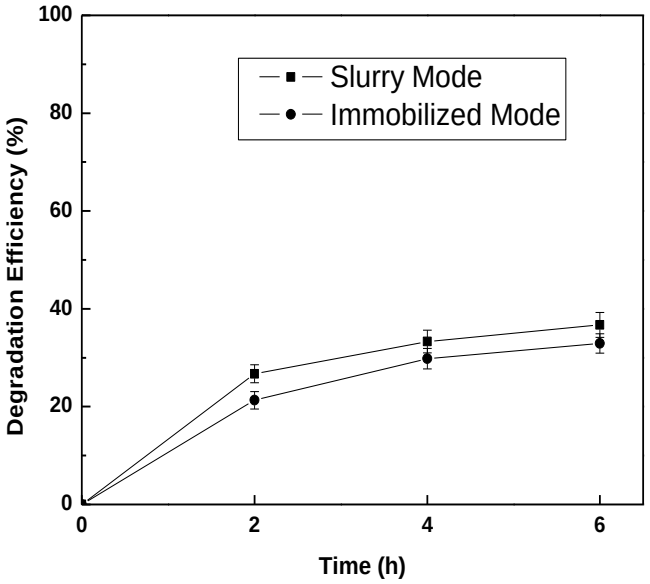


Fig. 4.42: Slurry and immobilization mode degradation of *Stage-2* effluent (ZnO dose: 1.5 g/L (slurry mode); Solar Irradiation time: 6 h)

The study, thus, demonstrates the degradation of model compounds, bleach mill effluents as well as combined pulp and paper mill effluents using photocatalyst under UV/solar light. The coupling of photocatalytic processes along with the biological processes was found to be effective in the degradation of the effluents. The applicability of the proposed process to treat actual bleach mill effluents (BME) depends strongly on the effluent's composition and concentration. The sequential anaerobic-aerobic-solar/ZnO-aerobic treatment was found to be most efficient in the degradation of pulp and paper mill effluents. Hence, photocatalysis can be introduced as part of the existing biological treatment (anaerobic followed by two stage aerobic treatment) as a viable industrial treatment for the complete degradation of the effluents.

5.0 DISCUSSION

This chapter deals with the interpretation and discussion of results on the heterogeneous photocatalytic degradation of various model organic compounds such as 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG). In addition, the degradation of bleach as well as combined pulp and paper mill effluents were studied for independent biological, photocatalytic and coupled treatment processes. The photocatalytic activity of catalysts like TiO_2 and ZnO in slurry mode was assessed for degradation of model compounds under UV/solar irradiation. The effect of various process parameters like catalyst dose, pH and oxidant concentration has been analyzed. An attempt has also been made to explore the possibility of utilizing mixed catalyst system for the photocatalytic degradation of 4-CG. Nanophotocatalysts were synthesized, characterized and their photocatalytic activity was evaluated using model compound (4-CG). The degradation efficiency/mineralization has been investigated in terms of changing concentration of the compound by measuring the absorbance or reduction in COD.

5.1 HETEROGENEOUS PHOTOCATALYTIC PROCESS

Heterogeneous photocatalysis is now considered as a promising approach for treatment of wastewaters and air. Photocatalysis refers to the oxidation and reduction reactions on semiconductor surfaces by the absorption of ultraviolet or visible light radiation. The method is widely being practiced for the degradation and mineralization of hazardous organic compounds to CO_2 and H_2O, reduction of toxic metal ions to their non-toxic states, deactivation and destruction of water borne microorganisms, decomposition of air pollutants like volatile organic compounds,

NO*x*, CO and NH_3, degradation of waste plastics and green synthesis of industrially important chemicals [Vinu and Madras, 2010].

5.1.1 Mechanism of photocatalysis

The following steps provide a detailed mechanism of photocatalytic degradation of organic compounds, which is well documented [Hoffmann et al., 1995; Bhatkhande et al., 2001]. While TiO_2 has been used as the semiconductor photocatalyst for the sake of representation, most of the following reactions are applicable for other semiconductor photocatalysts as well. The first step in the photocatalysis is the generation of valence band (VB) holes (h_{vb}^{+}) and conduction band (CB) electrons (e_{cb}^{-}), with the exposure of the semiconductor photocatalyst to UV radiation having energy greater than its band gap energy ($h\nu \geq E_{BG}$ of 3.2 eV). The holes mediate the oxidation of organic compounds by the formation of hydroxyl radicals, and the electrons mediate reduction and oxidation reactions by the formation of superoxide radicals [Kabra et al., 2004].

The other reaction possible at the catalyst surface is recombination of the generated (h_{vb}^{+} and e_{cb}^{-}) species and dissipate the input energy as heat. The photo generated holes that escape direct recombination reach the surface of TiO_2 and react with surface adsorbed hydroxyl groups or water to form trapped holes. The trapped hole is usually described as a surface-bound or adsorbed $OH^{\cdot}$ radical. Further both these entities can migrate to the catalyst surface, where they can enter in a redox reaction. In most cases the photogenerated holes react easily with OH^{-} or surface bound H_2O to oxidize them into $^{\bullet}OH$ radicals. The photo generated electrons could reduce organic substrate or react with electron acceptors such as O_2 dissolved in water, reducing it to superoxide radical anion $O_2^{\bullet -}$. Highly oxidant species (peroxide radicals) are also reported to be responsible for production of $^{\bullet}OH$ [Konstantinou and

Albanis, 2004; Daneshvar et al., 2003]. The fact is that the adsorbed aromatic compounds can undergo direct oxidation by electron transfer to the surface holes or react with electron donors in the solution to produce hydroxyl radicals. The overall process can be expressed by the following set of simplified equations:

$$TiO_2 + h\upsilon\ (UV) \rightarrow TiO_2\ (e_{CB}^- + h_{VB}^+) \qquad (5.1)$$

where *hv* is photon energy required to excite the semiconductor electron from the valence band (VB) region to conduction band (CB) region and e_{CB}^- is a conduction band electron and h_{VB}^+ is a valence band hole.

$$TiO_2\ (h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \qquad (5.2)$$

$$TiO_2\ (h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet \qquad (5.3)$$

$$TiO_2\ (e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \qquad (5.4)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet \qquad (5.5)$$

$$HO_2^\bullet + H^+ + TiO_2\ (e_{CB}^-) \rightarrow H_2O_2 + TiO_2 \qquad (5.6)$$

$$\text{Organic compound} + h_{VB}^+ \rightarrow \text{oxidation products} \qquad (5.7)$$

$$\text{Organic compound} + e_{CB}^- \rightarrow \text{reduction products} \qquad (5.8)$$

$$\text{Organic compound} + OH^\bullet \rightarrow \text{degradation products} \qquad (5.9)$$

Redox potential of $^\bullet OH$ radical is very high (□+2.8V), thus it is a powerful oxidizing agent and attacks organic compound present at or near the surface of TiO_2 to oxidize it. Metal oxides and sulphides represent a large class of semiconductor materials suitable for photocatalytic purposes. Among the various semiconductors, TiO_2 has been found to be the most widespread photocatalyst for environmental applications since TiO_2 is biologically and chemically inert; stable to photo and chemical corrosion and inexpensive [Linsebigler et al., 1995].

5.1.2 Process parameters of heterogeneous photocatalysis

The following process parameters have been identified that affect the effectiveness of the heterogeneous photocatalytic process. The parameters can be summed as:

- **Operational parameters**: pH, temperature, light intensity, light source (solar/artificial)
- **Catalyst parameters**: Nature of catalyst, catalyst dose, catalyst doping, mixed catalyst
- **Oxidant parameters**: Nature of oxidant, concentration of oxidant
- **Compound parameters**: Nature of pollutant, initial concentration

A brief outline on the effect of these parameters is discussed as follows:

5.1.2.1 Effect of catalyst

A semiconductor photocatalyst is characterized by an electronic band structure in which the highest occupied energy band called valence band (V_b) and the lowest empty band called conduction band (C_b) are separated by a band gap i.e. a region of forbidden energies in a perfect crystal. Some oxides and chalcogenides have enough band gap energies to be excited by UV or visible light and the redox potential of the edges of the V_b and C_b can promote a series of oxidative or reductive reactions. TiO_2 is so far the most useful material reported for photocatalytic process, owing to its exceptional optical and electronic properties, chemical stability, non-toxicity and low cost. The values for the flat band potential of the C_b and V_b of Degussa P-25 have been calculated as -0.3 and +2.9 V (pH=0), respectively [Martin et al., 1994]. The photocatalytic activity of various other catalysts such as ZnO, WO_3, CdS, ZnS and iron oxide has been also studied for the photocatalytic degradation of a wide variety of environmental contaminants [Neppolian et al., 2002]. ZnO has been found to be a

suitable alternative to TiO_2 and has been proved to be more efficient than TiO_2 in several applications [Lathasree et al., 2004; Abdullah et al., 2010].

5.1.2.2 Effect of catalyst dose

In the heterogeneous photocatalytic process, the degradation efficiency of substrate is directly related to the catalyst dose. There is a certain limit of catalyst dose beyond which the reaction rate becomes independent of catalyst dose and sometimes even decreases. The limit depends upon the surface characteristics of the semiconductor, nature of the compound to be treated and on the geometry and working conditions of the photoreactor corresponding to the maximum catalyst dose in which all the particles are totally illuminated.

The rate of photocatalytic degradation increases with increase in catalyst dose due to the fact that with increase in the catalyst dose, the number of organic molecules absorbed will increase owing to an increase in number of TiO_2 particles thereby enhancing the rate of photodegradation. The reason for decrease in photodegradation rate beyond a certain limit of catalyst dose may be explained in terms of screening effect of excess catalyst particles in the solution. The decrease in the penetration of light into the reaction volume makes part of the catalyst surface probably unavailable for photon absorption and hence photoactivated volume of suspension decreases resulting in decrease in degradation efficiency at higher catalyst loadings. [Hoffmann et al., 1995]. The substrate adsorption under such conditions brought little stimulation to catalytic reaction [Gao et. al., 2006]. Thus, an optimal concentration of the catalyst is necessary for the enhancement of the extent of degradation.

5.1.2.3 Effect of pH

The pH of the aqueous solution significantly affects the particle size, the surface charge, the band edge positions of the semiconductor and form of organic pollutant. The interpretation of pH effect on the efficiency of the photocatalytic

degradation process is a very difficult task because of its multiple roles. First, it is related to the acid base property of the metal oxide surface and can be explained on the basis of zero point charge. Second, hydroxyl radical can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels. Thirdly, organic pollutant may exist in different forms at acidic and alkaline pH. Bahnemann et al. (1991) has reviewed the acid–base property of the metal oxide surfaces can have considerable implications upon their photocatalytic activity. On the basis of zero point charge of TiO_2 and ZnO, the catalyst surface may get covered with chemically equivalent metal hydroxyl groups (M–OH) due to the adsorption of H_2O molecules at surficial metal sites and followed by the dissociation of OH^- groups. Due to the amphoteric behaviour of most metal hydroxides, the following two equilibria are considered:

$$M - OH + H^+ \rightarrow M - OH_2^+ \qquad K_1 \qquad (5.10)$$

$$M - OH \rightarrow M - O^- + H^+ \qquad K_2 \qquad (5.11)$$

The zero point charge (zpc) pH_{zpc} for TiO_2 (Degussa P25) is 6.8 and for ZnO is 9 [Sakthivel et al., 2002]. TiO_2 surface is positively charged in acidic media (Ph<6.8) whereas it is negatively charged under alkaline condition (pH>6.8). ZnO surface is positively charged below pH 9 based on their zpc.

5.1.2.4 Effect of oxidant concentration

The addition of an oxidant into a semiconductor suspension has been proven to enhance the rate of photooxidation of the organic pollutants [Naman et al., 2002; Poulios et al., 2000]. As discussed before, the photogenerated electrons and holes can recombine in the absence of a suitable scavenger.

5.1.2.5 Effect of initial substrate concentration

The degradation rate decreases with increase in initial concentration of the substrate. The possible explanation for this behaviour is that as the initial concentration of the compound increases, the path length of photons entering the solution decreases, resulting in retardation of penetration of light at sufficiently longer distances from light source. At low concentration the reverse effect is observed, thereby increasing the number of photons absorption by the catalyst in lower concentration [Davis et al., 1994]. Besides these parameters another important aspect of the photocatalyzed reactions is the adsorption of the organic compounds on the surface of the semiconductor particles. The Langmuir-type relationship between degradation rates and initial organic compound concentrations indicates that adsorption plays a role in the photocatalytic reaction. Generally, the degradation kinetics of compounds follows a Langmuir-Hinshelwood mechanism with a reaction rate varying proportionally to the fraction of surface covered by the substrate.

5.2 PHOTOCATALYTIC DEGRADATION OF 2-MP, 4-CC and 4-CG

The photocatalytic degradation of model compounds such as 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG) typically found in bleach mill effluents was performed in slurry mode under UV/solar irradiations. The photocatalytic activity of catalysts like TiO_2 / ZnO was assessed for degradation of 4-CC and 4-CG. The effect of various process parameters like catalyst dose, pH, oxidant concentration and initial substrate concentration has been examined. The degradation efficiency/mineralization was evaluated in terms of changing absorbance, reduction in chemical oxygen demand (COD) and high performance liquid chromatography (HPLC). Absorption measurement offers the convenient method to evaluate the degradation of model compounds as established previously [Doong et al.,

2001]. The disappearance of the peaks indicated the gradual degradation of the model compound.

The weak disappearance of 2-MP, 4-CC and 4-CG in the absence of catalyst is assigned to the direct photolysis resulting in weak UV light absorption by the model compound however; heterogeneous photocatalytic treatment is more effective in the degradation of model compounds as compared to photolysis. The results are in agreement with the previous reported observations on photolytic and photocatalytic degradation of substituent phenolic compounds [Kansal et al., 2007].

5.2.1 Effect of operating parameters

ZnO appeared to be better photocatalyst than TiO_2 for the degradation of the model compounds. In 4-CG, ZnO mediated phototreatment attained significantly higher degradation efficiency as compared to TiO_2. Literature studies also emphasized that the quantum efficiency as well as the photocatalytic efficiencies of ZnO powder is significantly larger than that of TiO_2 powder [Richard et al., 1992]. The important advantage of ZnO is its potential to absorb over a larger fraction of solar spectrum than TiO_2 [Sakthivel et al., 2003]. The result is in confirmation with earlier findings wherein ZnO was used as an alternative to TiO_2 for the photocatalytic degradation of novel compounds and the proposed mechanism of degradation for TiO_2 and ZnO is same [Daneshvar et al., 2003; Pirkannicmi and Sillanpaa, 2002].

The amount of catalyst plays an important role in the degradation of the organic compound in photocatalysis. Selection of optimum catalyst concentration is important in order to minimize excess use of catalyst and to ensure total absorption of photons. The effect of catalyst dose was studied by varying TiO_2 dose from 0.5 to 3.0 g/L for the degradation of 2-MP (25 mg/L) at pH (6.7) for 5 h of UV exposure**.** The decrease in absorbance at λ_{max} was considered as an index of degradation. With the increase in TiO_2 dose to 2.0 g/L, the degradation efficiency enhanced to 86.7%,

beyond which the efficiency declined. For the degradation of 4-CC (50 mg/L), the photocatalytic experiments were performed by varying TiO_2/ ZnO dose from 1.0 to 3.0 g/L at pH 6.5. The maximum degradation of 87.4 and 82.8% was achieved with 2.5 g/L TiO_2 after 6 h and 1.5 g/L ZnO after 2 h of UV exposure, respectively. However, the extent of degradation was observed to reduce with increasing dosages of TiO_2 and ZnO beyond 2.5 and 1.5 g/L, respectively. Similarly for the photocatalytic degradation of 4-CG (25 mg/L), the experiments were performed by varying TiO_2/ ZnO dose from 1.5 to 3.0 g/L at pH 6.75 under UV irradiation for 6 h. The maximum degradation of 47.6 and 75.4% was achieved with 2 g/L TiO_2/ ZnO at pH (6.75) after 6 h of UV irradiation. However, increasing catalyst dose beyond 2 g/L, reduced the extent of degradation. The extent of degradation increases with increase in catalyst dose which is presumably due to increase in the active sites for adsorption of the compound on the catalyst surface as well as the enhanced generation of free hydroxyl (*OH) radical, indicating a heterogeneous catalytic regime [Sakthivel et al., 2003]. However, further increase in catalyst dose decreased the degradation efficiency which may be due to increase in turbidity of the suspension that increases light scattering and a screening effect reduces the specific activity of the catalyst [Akyol et al., 2004].

The amphoteric behaviour of most semiconductor oxides influences the surface charge of the photocatalyst. It is well known that pH can affect the mechanism and routes of degradation. The TiO_2 point of zero charge (pzc) is between pH 5.6 and 6.8 [Ho and Bolton, 1998]. Hence, depending on the pH the catalyst surface will be either be charged positively (for pH < pzc), negatively (for pH > pzc) or remain neutral (for pH ≈ pzc). This characteristic significantly affects the adsorption and desorption properties of TiO_2. In addition, the structure of the pollutants is also influence by change in pH. For instance, 4-CC and 4-CG has a pKa value of 6.5 and 6.75 respectively and can be charged either positively or negatively on basis of the

pH. The maximum degradation of 2-MP (25 mg/L) was observed at with 2.0 g/L TiO_2 at pH 6.0. The maximum degradation of 4-CC (50 mg/L) was achieved with 2.5 g/L at pH of 6.5 whereas 2.0 g/L TiO_2 at pH of 6.75 were the optimal conditions for the degradation of 4-CG (25 mg/L). This observation is due to the more pronounced adsorption of organic compound in the acidic range than in the alkaline range which is expectedly due to the more adsorption of organic compound in this pH range. It seems clear that the interaction and affinity between both species will be different relying on the pH. The similar behaviour is also documented in some of the research findings on efficiency of photocatalysts under varying pH conditions [Auguliaro et al., 1991]. Hence, pH of 6.5 and 6.75 was chosen to be an optimum pH for photocatalytic degradation of the aqueous solution of 4-CC and 4-CG respectively.

For the degradation of the model compounds in the presence of ZnO, the maximum degradation for 4-CC and 4-CG was 98.6 and 92.7% with 1.5 g/L ZnO at pH 8 and 2.0 g/L ZnO at pH 10 respectively. The behaviour is attributed to the fact that variation in pH entails an alteration in the properties of semiconductor-liquid interface, mainly related to acid base equilibrium of the adsorbed hydroxyl group. The formation of hydroxyl radical from OH^- is favoured at high pH due to the presence of large quantity of OH ions in the alkaline medium. Abdullah et al. (2010) observed similar behaviour in their studies. The zero point charge (zpc) pH_{zpc} for ZnO is 9 [Neppolian et al. 1998]. ZnO surface is positively charged below pH 9 based on their zpc. This observation is further supported by earlier report on photocatalytic degradation of lignin using TiO_2 and ZnO semiconductors wherein maximum photocatalytic degradation of lignin was attained at pH value of 11 using ZnO [Kansal et al., 2008]. Moreover, ZnO gets dissolved in the acidic medium.

Addition of sodium hypochlorite as an oxidant along with TiO_2 (2.5 g/L) at pH of 6.5 and TiO_2 (2.0 g/L) at pH of 6.75 for the photocatalytic degradation of 4-CC and

4-CG, respectively was observed to improve the rate of photodegradation in the initial phase or alternatively reduced the time required for degradation. A reason for this could be the availability of hypochlorite ion (OCl-) which is unstable and ultimately degrades to chloride and chlorate ions resulting in oxidation of more organic matter. The increase in the concentration of NaOCl beyond specified limit may be contributing towards the slight increase in COD value due to more consumption of potassium dichromate by hypochlorite ion. Similar trend was also observed for photodegradation of chlorophenols by using UV/TiO_2 in presence of inorganic oxidant perchlorate [Pandiyan et al., 2002]. The addition of NaOCl as an oxidant with ZnO did not show any improvement in the degradation efficiency of 4-CC and 4-CG.

The TiO_2 mediated photodegradation efficiency of 2-MP, 4-CC and 4-CG in the presence of solar light was found to be in close proximity to UV light under optimized conditions which is due to their ability to absorb part of the visible light. The ZnO mediated degradation of 4-CC and 4-CG in solar light was more than that observed under UV irradiation, thus demonstrating the efficacy of solar irradiation as a cost-effective approach to achieve photocatalytic degradation of model compounds. Sakthivel et al. (2003) also emphasized that ZnO has ability to absorb over a larger fraction of solar spectrum than TiO_2. Karunakaran and Senthivelon (2005) also showed better photocatalytic oxidation of aniline in solar light.

As the initial concentration of the solution was increased, the degradation efficiency was found to decrease. Alternatively, for the higher initial load concentrations, total degradation was achieved with longer irradiation times. In the dilute 4-CG solution, the rate of production of hydroxyl radical (*OH) increased because of increased incidental photonic flux irradiating the catalyst, which subsequently allow the degradation to be faster. This can be explained on the basis of the fact that as the initial concentration increases, more and more organic substances

are adsorbed on the surface of photocatalyst, therefore, reducing the generation of hydroxyl radicals since there are only a fewer active sites for adsorption of hydroxyl ions and the generation of hydroxyl radicals. Further, as the concentration of the substrate is increased, the photons get intercepted before they can reach the catalyst surface, hence decreasing the absorption of photons by the catalyst, vis-à-vis the degradation efficiency [Wu et. al., 2004; Qamar et. al., 2005; Daneshvar et. al., 2004]. Previous study also reported the degradation of 2,4,6-trichlorophenol as a function of irradiation time and noticed that extent of degradation was higher for the weaker concentration of organic compound solutions [Ochuma et al., 2007].

5.2.2 Reaction kinetics

The reaction kinetics tells the rate at which photocatalytic reaction proceeds. The kinetics of photodegradation has been explained with respect to 4-CC:

$$HO_{ads}\bullet + \text{4-CC} \rightarrow \text{Intermediates}_{ads} \rightarrow \text{Intermediates}_{free} \qquad (5.12)$$

$$HO_{ads}\bullet + \text{Intermediates} \rightarrow CO_2 + H_2O + Cl^- \qquad (5.13)$$

If we presume that that reaction (1) is of a first-order relating to 4-CC/4-CG concentration, keeping the hydroxyl radicals concentration constant, the degradation rate r would be governed by the equation:

$$r = d[\text{4-CC}]/dt = K_{(\text{4-CC})}[HO_{ads}\bullet]^{\alpha}[\text{4-CC}] = K_{app}[\text{4-CC}] \qquad (5.14)$$

where α is the reaction order relating to the adsorbed hydroxyl radicals concentration, $K_{(\text{4-CC})}$ is the real rate constant and K_{app} is the apparent rate constant of the degradation of 4-CC. The above equation can further be solved as follows:

$$\ln[\text{4-CC}]_0 / [\text{4-CC}] = K_{app}\, t \qquad (5.15)$$

where $[\text{4-CC}]_0$ and [4-CC] are respectively the concentrations of 4-CC at time 0 and t. The straight lines $\ln[\text{4-CC}]_0$ / [4-CC] vs. time were in agreement with a pseudo first-order degradation of 4-CC. The apparent rate constant for degradation of 4-CG was more with ZnO (0.447 h^{-1}) as compared to TiO_2 (0.115 h^{-1}) which implies

that ZnO was more effective in the degradation of 4-CG as compared to TiO_2. The degradation of 4-CG was observed to be of pseudo first-order rate. Similar behaviour has been documented in the photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide and degradation reaction was found to follow pseudo-first order kinetics [Wang et al., 1999].

5.2.3 Mineralization studies

The degradation of the 2-MP was also recorded in terms of COD reduction. The maximum COD reduction from 144 to 10 mg/L was observed with 2.0 g/L TiO_2 at pH 6.0 during the photocatalytic process. The decrease in COD of the solutions further strengthens the observation that the degradation of the sample was occurring, as observed by Pérez et al. (2002).

5.2.4 HPLC studies

HPLC chromatographs obtained during photocatalytic degradation of aqueous solution of 4-CC (50 mg/L) and 4-CG (25 mg/L) depicts the decrease in the characteristic peak of 4-CC and 4-CG at retention time of 3.527 and 5.1 min., which further confirmed their degradation. Simultaneously, chromatographs observed after photocatalytic treatment of 4-CC showed the appearance of few intermediates and photodegradation of 4-CG also witnessed intermediate at a retention time of 2.8 min. The concentration of the intermediate was increasing with the extent of photocatalytic reaction of 4-CG. The identification of the intermediate is future course of study. The formation and identification of intermediates during photocatalytic degradation of commercial dye-Procion blue HERD from real textile wastewater was reported (Bansal and Sud, 2011).

5.2.5 Efficacy of the recycled catalyst

The photocatalytic process should be economical so that it is successfully applicable at the industrial scale and the role of catalyst's lifetime is an important parameter which makes the process cost effective. The results of catalyst recycling with ZnO under optimized conditions depict that the catalyst was effectively recycled for at least four times in the degradation of 4-CG, but with 15% reduction in the degradation efficiency in each cycle. Catalyst fouling and loss of catalyst during filtration is the major cause behind the drop in the efficiency of the catalyst. The similar findings have been reported in the degradation of textile wastewater for biodegradability enhancement by Dubey et al. (2009).

5.3 PHOTOCATALYSIS USING MIXED/ HETEROSTRUCTURED NANOPHOTOCATALYSIS

5.3.1 Photocatalytic degradation of 4-CG using mixed photocatalysts

The heterogeneous photocatalytic process was studied using mixed photocatalyst having ZnO and TiO_2 in different proportions and results depict more degradation efficiency as compared to individual catalyst. The possible reasons may be simultaneous photo excitation of the photocatalysts and quickly passing the electrons to the substrate molecules thereby preventing the reunion of electrons and hole pair, which triggers the various reactions leading to the degradation of the compound. Similar findings have been reported for the degradation of acid orange 7 (AO7) dyes with mixed catalyst [Bansal, 2011].

The degradation in the presence of solar irradiation was found to be more when compared to UV irradiation. The results are in agreement with the earlier findings [Sakthivel et al., 2003], that ZnO can harvest maximum solar energy by utilizing visible light for degradation of water bound organics. Although sunlight has only 5% of optimum energy for photocatalytic excitation as well as for degradation of

pollutants, it is a safe and cost effective irradiating source. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries like India, intense sunlight is available throughout the year and, hence it could be effectively used for photocatalytic degradation of pollutants in wastewater. Moreover there is no material deterioration in case when sunlight is used as a radiation source.

5.3.2 Degradation of 4-CG using synthesized heterostructured nanophotocatalysts

The characterization of heterostructured ZnO/TiO_2 nanophotocatalysts was done with X-ray diffraction, SEM and UV–DR spectra. The nanophotocatalyst was prepared in molar ratio of 9:1 (Z_9T). From the XRD pattern and corresponding characteristic 2θ values of the diffraction peaks, it can be confirmed that TiO_2 is in rutile form having tetragonal structure as the peaks matched with Joint Committee Powder Diffraction Standards (JCPDF) card number 21-1276 while ZnO is in zincite phase (JCPDF card number 36-1451). The low intense peaks of TiO_2 observed in the XRD pattern of Z_9T are due to small proportion of TiO_2. However, the presence of ZnO and TiO_2 peaks in photocatalysts (Z_9T) show that the phase composition is the mixture of ZnO and TiO_2.

The average crystallite size of samples was calculated to be about 21.48 nm using the Scherrer equation [Tian et al., 2009].

$$t = K\lambda / B\cos\theta \qquad (5.16)$$

Where K is coefficient = 0.9, λ = 0.1541 nm, B is the full width half maximum (FWHM) of the catalyst and θ is the diffraction angle. The energy band gap of sample has been calculated according to the equation widely adopted for crystalline semiconductors [Fu et al., 2006; Maruyama et al., 2006].

$$\alpha h\upsilon = A\,(h\upsilon - Eg)^{(n/2)} \qquad (5.17)$$

Where α, υ, A, Eg and n are the absorption coefficient, incident light frequency, constant, band gap, and an integer (normally equal to 1, 2, 4, or 6), respectively. The α and υ values at the steep edges of the transmission spectra were used to construct the plots of $(\alpha h\upsilon)^{1/2}$ against photon energy.

The better degradation efficiency of Z_9T in the degradation of 4-CG may be explained on the basis of smaller crystallite size (21.48 nm). When the catalyst grain size is reduced down to a few nanometres, an elevated density of active sites for substrate adsorption and/or catalysis can be guaranteed, as small crystallite size possess significantly higher surface-to-volume ratio as compared to the bulk material. Previous work [Xu et al., 1999] has also confirmed that the concentration of model solution decreased more rapidly with a decrease in the crystallite size of photocatalysts. The higher photocatalytic activity of ZnO/TiO_2 nanophotocatalyst is also related to the vectorial transfer of electrons and holes, which takes place in coupled semiconductors possessing different redox energy levels for their corresponding conduction and valence bands the electron transfer occurs from the conduction band of light-activated ZnO to the conduction band of light-activated TiO_2 and, conversely, hole transfer can take place from the valence band of TiO_2 to the valance band of ZnO. This efficient charge separation increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates [Sukharev and Kershaw, 1996].

5.4 TREATMENT OF BLEACH MILL EFFLUENTS

The research work was carried out in order to assess the optimal conditions in which the effluent from different bleaching sections of the pulp and paper mill can be treated so that the degradation of xenobiotics discharge takes place. The high chemical oxygen demand (COD) of both C and E_1 stage effluents showed the

presence of significant levels of organic and inorganic constituents in the effluents. The high chloride content in the effluent prevents its recycling since its accumulation in the closed circuit poses choking problems in the fluidized bed recovery of black liquor. The release of these effluents into water bodies with high COD and TDS values can cause damage to the aquatic environment; hence its treatment is inevitable for the discharge of effluents. Thus, biological as well as photocatalytic treatment of the C and E_1 effluents were performed. From the results of the preliminary studies, an attempt was made to develop industrially viable treatment system involving coupled treatment with biological treatment as a preliminary or post photocatalytic treatment.

5.4.1 Biological treatment of C and E_1 effluents

The results indicate that most of the biodegradable compounds present in the effluent were degraded within 24 h (30% for C and 57% for E_1 effluent), beyond which the major proportion of the constituents present in the effluent were non-biodegradable or hardly biodegradable substances. This is the reason why the enhanced degradation was not achieved even with higher retention periods of 5 days.

5.4.2 Photocatalytic treatment of C effluent

In order to investigate the photolysis of effluent in the presence of ultra-violet radiations, the effluent was subjected to UV irradiation in the absence of photocatalyst and results showed negligible degradation of 4.6% which is due to the weak UV light absorption by the effluent. The degradation efficiency was marginally higher (12%) in the presence of catalyst but in the absence of light (dark/TiO_2 system), which may be attributed only to adsorption of the pollutants on the surface of the photocatalyst. The degradation efficiency of effluent was also observably insignificant in the presence of NaOCl as oxidant in UV irradiation. Comparatively, photocatalysis (UV+TiO_2) resulted in more degradation of the effluent samples when compared to photolysis.

The literature also supports that advanced oxidative treatment of bleaching effluent removes the organic content of the waste rapidly [Yeber et al., 1999].

There is a relationship between the amount of catalyst used and the degradation efficiency and maximum extent of degradation was achieved with 3 g/L and 2.5 g/L TiO_2 and ZnO respectively which may be due to increase in availability of more active sites on the catalyst surface. Further increase in catalyst dose, beyond specified limit, reduced degradation due to increase in the turbidity of the suspension and hence, photoactivated volume of suspension decreases [Yeber et al. 1999] as noted in previous study. The degradation efficiency achieved was higher with ZnO as compared to TiO_2 which is in agreement with previous findings [Tennakone et al., 1992; Sakthivel et al., 2003].

The variation of pH showed that the maximum degradation efficiency was 42.6% and 54.5% obtained with 3.0 g/L TiO_2 at pH 6.0 and 2.5 g/L ZnO at pH 8.0, respectively. Moreover, there were no significant changes in pH during the course of degradation. The higher degradation was observed with TiO_2 at pH 6 may be explained on the basis of more pronounced adsorption of organic compound in the acidic range than in the alkaline range [Behnemann et al., 1991]. However, the ZnO catalyzed degradation reactions were rapid at alkaline pH of 8.0 due to zpc of ZnO. The similar research findings have been reported in case of degradation of lignin wherein ZnO showed higher degradation of lignin in alkaline pH [Kansal et al. 2008].

The enhanced degradation of the C stage effluent with TiO_2/NaOCl could be because of the availability of hypochlorite ion (OCl^-) which is unstable and ultimately degrades to chloride and chlorate ions resulting in oxidation of more organic matter. The presence of oxidant in case of ZnO did not result in any increase in degradation efficiency of C effluent and rather a decrease in degradation efficiency was observed at higher doses of NaOCl which could be explained on the fact that increase in the

concentration of NaOCl may be contributing towards the marginal increase in COD levels due to higher consumption of potassium dichromate by hypochlorite ion. The present results are also in agreement with the observations of other researchers [Kansal et al. 2009], in this context.

The degradation efficiency of C effluent in both UV and solar mode under optimized conditions depicts that degradation in solar irradiation was found to be similar to that attained in the UV light with no statistically significant difference. This observation correlated with the previous work wherein the photodegradation of pulp and paper mill effluent gave comparable results in both UV and solar light [Toor et al., 2006]. These observations demonstrate the efficacy of solar irradiation as a cost-effective approach to achieve photocatalytic degradation of effluent which is nearly similar to that of observation with UV as radiation source.

5.4.3 Photocatalytic treatment of E_1 effluent

Direct photolysis has not been found to be effective in the degradation of E_1 effluent as observed previously with C effluent. In the absence of light, less degradation efficiency has been observed which accounts for adsorption of the effluent onto the catalyst surface. The degradation efficiency is in accordance with the earlier reported studies on photodegradation of bleaching effluents [Yeber et al., 2000]. The degradation efficiency of E_1 effluent increased when increasing the TiO_2 and ZnO loading up to 2.5 g/L. However, further increase in catalyst loading did not lead to higher degradation efficiency which may be due to an increase in light scattering and decrease in photoactivated volume of suspension. ZnO has been observed to have higher efficacy of treatment as compared to TiO_2.

The experimental study related to the effect of variation of pH depicts that the maximum extent of degradation was 26% and 44.5% which was achieved with 2.5 g/L TiO_2 at pH 4.0 and 2.5 g/L ZnO at pH 8.0, respectively. This observation in case

of TiO_2 is due to the more pronounced adsorption of organic compound in the acidic range than in the alkaline range [Vinu and Madras, 2010].

The addition of oxidant enhanced the degradation efficiency of C-stage effluent samples with TiO_2. Addition of sodium hypochlorite as an oxidant with ZnO (2.5 g/L) at pH 8 did not improve the degradation efficiency of effluent. Literature reported earlier had also shown insignificant effect of addition of NaOCl in the presence of ZnO on the degradation efficiency [Kansal et al. 2009].

The effect of UV/solar irradiation on the degradation efficiency of under optimized conditions has shown relatively closer degradation efficiency in solar mode to that observed under UV irradiation after 6 h of exposure. Earlier reported study also gave comparable results of photocatalysis in the treatment of wastewater under UV or solar irradiations [Oller et al. 2007]. So solar light can be utilized alongwith ZnO for the treatments of effluents at an industrial scale.

The applicability of the proposed process to treat actual BME depends strongly on the effluent's composition and concentration. The effluent needs to be separated from its solid content and then diluted several times prior to photocatalytic treatment in order to achieve practically significant treatment efficiencies. This implies that photocatalysis may be part of a process sequence for the effective treatment of such type of industrial effluents.

5.4.4 Integrated treatment of C effluent

The use of biological treatment is attractive due to its low operating cost but the residence time is high. On the other hand, the degradation rate of advanced oxidation processes is high but the operation is relatively expensive due to the use of reagents and irradiation sources. Hence, the integration of AOPs with existing biological processes would help in enhancing degradation, reducing residence time and moderating operating costs. The sequential process involving photocatalysis

(TiO_2/ZnO) followed by biological treatment (Photo+Bio) and the reverse sequential treatment (Bio+Photo) were applied to C effluents. Due to low biodegradability of C effluent, this physiochemical pre-treatment is necessary to modify the pollutants present in the effluent into easily biodegradable intermediates. This allows the subsequent biological degradation to be achieved in a short time and more economical way. The optimal time required for phototreatment corresponds to the best compromise between the efficiency of phototreatment and the cost. Hence ZnO mediated solar photocatalytic (1 h) – biological (12 h) sequential treatment (Photo+Bio) was found to be efficient and cost effective in the degradation of C effluent due to attainment of high degradation efficiency (91.6%), application of inexpensive solar light and decreased residence time in biological treatment. TOC removal was higher for sequential photocatalytic (solar/ZnO) – biological treatment as compared to reverse treatment sequence which further substantiates that solar induced photocatalysis with ZnO followed by biological treatment showed better efficacy for the degradation of C effluent. The previous researchers also documented the enhanced degradation of organics by application of photocatalytic treatment prior to biological treatment when compared to individual processes [Reyes et al. 1998; Tamer et al. 2007].

5.4.5 Integrated treatment of E_1 effluent

The sequential photocatalytic followed by biological treatment (Photo+Bio) and reverse treatment processes (Bio+Photo) were employed for the degradation of E_1 effluent in terms of COD reduction. The results show that sequential biological (24 h) – solar/ZnO (2 h) resulted in 95.4% degradation as compared to 84.8% degradation which occurred with sequential solar/ZnO (2 h) - biological treatment (24 h). So the highest degradation efficiency was achieved for biologically pretreated E_1 effluent followed by photocatalytic treatment (solar/ZnO). The application of biological

treatment resulted in degradation of organic compounds present in the effluent and at the same time, facilitating the conversion of functional groups to more easily oxidizable forms which may subsequently be degraded during photocatalytic treatment. The photocatalytic degradation efficiency was also studied in terms of TOC reduction. Comparatively less TOC reduction was observed with biotreatment or photocatalytic treatment systems alone whereas, significant TOC reductions were observed with sequential (Bio+Photo) processes. Hence, ZnO mediated solar photocatalytic treatment may be applied after biological treatment to achieve higher degradation efficacy for E_1 effluent. The application of photocatalytic oxidation to biotreated kraft bleaching effluents has been reported to degrade the xenobiotics present in the effluents [Balcioglu and Arslan, 1998].

5.4.6 GC-MS studies

The degradation of the organics was established by performing the gas chromatographic studies. Comparison of the chromatograms clearly reveals the degradation of the substituent phenolic compounds and specifically the targeted model compound present in the real bleach mill effluents. Further, ZnO exhibits better photocatalytic activity than TiO_2 even in the degradation of real bleach mill effluents. Previous report on GC-MS studies also documented the degradation of dye with the photocatalytic treatment [Troupis et al., 2009].

5.5 TREATMENT OF COMBINED PULP AND PAPER MILL EFFLUENTS

In order to attain complete degradation of the combined pulp and paper mill effluents, the independent photocatalytic and sequential photocatalytic-biological treatment was employed to effluents from different stages of functional ETP. For instance, the *raw* effluent (primary clarified), *stage-1* (UASB treated) and *stage-2* (sequential UASB-ASP-I treated) were subjected to photocatalytic treatment alone.

Similarly, sequential photocatalytic-biological treatment was employed for the *stage-1* and *stage-2* effluents so as to form coupled treatment train namely anaerobic-photocatalytic-aerobic and anaerobic-aerobic-photocatalytic-aerobic sequence, respectively. In order to combine biological process as the post photocatalytic treatment, the solution biodegradability must be improved during photocatalysis so that it can be fed to subsequent biological treatment, else more oxidation may be needed. Previous study has also emphasized on the enhancement of BOD/COD during the photocatalytic treatment [Parra et al., 2000].

5.5.1 Photocatalytic treatment

Photocatalytic treatment was employed for *raw*, *stage-1* and *stage-2* effluents with TiO_2 or ZnO under UV light. ZnO was found to be a better photocatalyst than TiO_2 in the degradation of pulp and paper mill effluents. Moreover, ZnO showed higher efficacy in the presence of solar irradiation as compared to TiO_2. Initially, the photocatalytic activity increased with increase in dose of photocatalyst which may be due to increase in availability of more active sites on surface of catalyst. However, further increase in catalyst dose beyond certain limit depending upon the type of catalyst reduced the extent of degradation which is presumably due to reduced photoactivation caused by increased turbidity of the suspension. The degradation efficiency is in accordance with the earlier reported studies on photodegradation of black liquor and textile mill effluents [Peralta-Zamora et al., 1998]. Keeping this in view, detailed biodegradability studies were carried with ZnO as a catalyst under solar light.

5.5.2 Sequential photocatalytic-biological treatment of *stage-1* effluent

In the integration of photocatalysis and biological processes, the main responsibility of photocatalytic process is to enhance the biodegradability of the wastewater by partial oxidation and the complete oxidation/mineralization occurs with

subsequent low cost biological method. The *stage-1* (53% degradation in UASB treatment of ETP) effluent was subjected to photocatalysis followed by aerobic treatment in order to affect integrated anaerobic-photocatalytic-aerobic sequential treatment. In the anaerobic treatment carried out at functional ETP, a large portion of COD was removed from the effluent. Then in photocatalytic treatment, non-biodegradable residuals are decomposed to smaller and more biodegradable molecules which are suitable for aerobic treatment in the final stage. It is therefore desirable to increase the biodegradability of wastewater in the photocatalytic stage as much as possible. The results reveal that 2 h pretreatment time with solar/ZnO was observed to be necessary for *Stage-1* effluent sample to enhance its biodegradability from 0.38 to 0.56 so that the same can be treated efficiently in subsequent biological treatment. These observations are further supported by earlier studies wherein an enhanced biodegradability was reported post photocatalytic treatment [Sarria et al., 2002]. The degradation of 87.8 and 89.9% was achieved with anaerobic-solar/TiO_2-aerobic and anaerobic-solar/ZnO-aerobic integrated systems, respectively. The coupled system that involved anaerobic ➔ photocatalytic ➔ aerobic approach observably has better efficacy in removal of organics than the conventional anaerobic-aerobic sequential treatment.

5.5.3 Sequential photocatalytic-biological treatment of *stage-2* effluent

The *stage-2* effluent sample which was subjected to sequential anaerobic-aerobic-I treatment in the industrial ETP (having degradation of 84% w.r.t. initial COD) was further treated photocatalytically before aerobic biological treatment. The sequential photocatalytic-biological treatment as applied to *stage-2* effluent resulted in the maximum extent of degradation with ZnO under solar light. In order to combine chemical process outlet with biological process, it is necessary to determine the variation of biodegradability as a function of the photochemical reaction. The

biodegradability enhanced to 0.18 and 0.2 after 1 and 2 h of photocatalytic (solar/ZnO) treatment, respectively. In general, 1 h of photo treatment (solar/ZnO) followed by 12 h of aerobic biological treatment of *stage-2* effluents has been found to be optimal for achieving significant overall degradation of 97%. In integrated anaerobic-aerobic-photocatalytic-aerobic approach, the first two biological stages resulted in reduction of BOD and COD of the effluent following which photocatalysis removed biorecalcitrant compounds and further biological treatment served as a polishing stage for post-treatment of residuals. Observations further strengthen the revelations that coupled treatment removed most of the biodegradable and non-biodegradable organics from the effluent and the discharge values were quite low. This is further supported by studies reported earlier wherein COD reduction of 86% was observed with sequential treatment of pulp and paper mill effluents in pilot scale bioreactor [Singh, 2007]. Multi-stage integrated photocatalytic-biological treatment is advantageous for biorecalcitrant and inhibitory wastewater streams for decreasing the operating cost of the treatment. As the functional ETP consists of UASB followed by two stage ASP, photocatalysis can be introduced after ASP-1 to affect sequential anaerobic➔aerobic➔Solar/ZnO➔aerobic sequence. This coupled treatment was observed to be most efficient (with a degradation efficiency of 97%) and optimally viable treatment protocol in the existing ETP for enhanced degradation of the pulp and paper mill effluents.

5.5.4 Supported photocatalyst in the treatment process

In order to enhance the viability of the coupled system, further the photo-treatment step was attempted with immobilized catalyst (ZnO) under solar radiation for the degradation of *stage-2* effluent. The advantages of using supported catalytic system is that: (i) the catalyst can be reused; (ii) catalyst separation is not required; (iii) ease of cleaning after use followed by drying of immobilized matrix under

sunlight; and (iv) pH of the solutions remain neutral. The degradation achieved in immobilized mode was less as compared to slurry mode but still it suggests an economical approach in use of catalyst in photodegradation. These observations are also supported by earlier reports available in literature [Kansal et al., 2008], wherein ZnO applied in immobilized mode showed less degradation efficacy as compared to slurry mode. So the coupled treatment involving photocatalysis in immobilized mode may be viable technology at industrial level as the filtration of the effluent can be avoided.

6.0 CONCLUSION

The present study involves the cost effective solutions to treat pulp and paper mill effluents containing chlorinated substituted organics. The degradation of bleach as well as combined pulp and paper mill effluents was examined by coupling heterogeneous photocatalytic processes with conventional biological treatment. An attempt was made to introduce photocatalytic treatment as a part of the existing biological treatment (anaerobic followed by two stage aerobic treatment) being adopted in industrial ETP so as to maximize the degradation efficiency of combined pulp and paper mill effluents with little modifications and minimum input cost. The fixed catalyst approach was also evaluated for *stage-2* effluents using ZnO under solar mode. The C and E_1 stages bleach mill effluents were also subjected to independent biological, photocatalytic and coupled treatment systems. Photodegradation of the model compounds such as 2-methoxy phenol (2-MP), 4-chlorocatechol (4-CC) and 4-chloroguaiacol (4-CG) typically found in bleach mill effluent were performed using different photocatalysts under UV/solar light irradiations. The outcomes of the present study are summarized as follows:

- Heterogeneous photocatalytic degradation is a viable alternative for the degradation persistent organic contaminants in water. This promising technology solves the problem of transforming recalcitrant organic contaminants to non-persistent substance.
- Photocatalytic degradation of all model compounds (2-MP, 4-CC and 4-CG) and real effluents was facilitated by the presence of catalyst. The degradation efficiency was found to be insignificant during photolysis. Experimental results indicated that initial rate of photodegradation of each compound

increased with increase in catalyst dose upto an optimum loading. The rate of photocatalytic degradation was strongly influenced by the pH of the solution.

- Comparison of the photocatalytic activity of TiO_2 and ZnO under UV/solar light indicated ZnO to be better degrading catalyst than Degussa P25 TiO_2 for the degradation of the model compounds and effluents. Moreover photocatalytic activity of ZnO was better in the presence of sunlight as compared to UV light.
- In case of TiO_2, use of sodium hypochlorite as an oxidant enhanced degradation efficiency however, NaOCl showed no effect in case of ZnO.
- The initial rates of photodegradation were high at lower concentrations of model compounds such as 2-MP and 4-CG.
- The reaction rate for the degradation of 4-CC and 4-CG was found to be pseudo-first order with respect to their concentration within the experimental range. Photodegradation kinetics was described by the Langmuir-Hinshelwood model.
- The COD/HPLC analysis of different model compounds revealed significant reduction in their COD value /characteristic peak with respect to their initial values, indicating the degradation of recalcitrant organic compounds.
- The efficiency of photocatalytic degradation was found to be increase when both the catalysts; ZnO and TiO_2 were employed in the ratio of 9:1 for degradation of 4-chloroguaiacol (4-CG).
- Synthesized heterostructured ZnO/TiO_2 photocatalysts (Z_9T) have TiO_2 phase in rutile form having tetragonal structure while ZnO is in zincite phase. The photocatalytic efficiency of Z_9T was more than ZnO (Merck) and Degussa P25 TiO_2 for the degradation of 4-CG at pH 10.

- The independent biological and photocatalytic treatment applied for the degradation of C and E_1 stages of soda bleaching effluents from an agro residue based pulp and paper mill revealed that none of the biological or photocatalytic treatment was sufficient to completely degrade the organics present in the BME.
- Qualitative and quantitative analysis of model compounds in C stage bleach mill effluents was evaluated using GC/MS technique and chromatograms confirmed the degradation of model compounds in C stage bleach mill effluent.
- Due to the low biodegradability of C effluent, the photocatalytic pretreatment was necessary and the minimum pretreatment time required to increase biodegradability was identified.
- The sequential solar/ZnO (1 h) - biological treatment (12 h) was more effective in the reduction of Total Organic Carbon (TOC) of the C effluent, however, sequential biological (24 h) – solar/ZnO (2 h) was more effective for E_1 effluent.
- It is evident from the present study, that the coupling of solar assisted AOP - biological treatment processes or *vice versa*, based on the type of the effluent, prove beneficial over the either of the treatment systems independently, in reducing COD/TOC load.
- The photocatalytic treatment of *raw, stage-1* and *stage-2* effluent samples from the functional Effluent treatment plant (ETP) of agro-residue based pulp and paper mill carried out with TiO_2 and ZnO indicate ZnO to possess better photocatalytic activity than TiO_2 and moreover, solar induced degradation was comparative to degradation under UV light.

- Integration of existing biological processes (anaerobic followed by two stage aerobic treatment) with photocatalytic treatment was observed to be more efficient in the treatment of pulp and paper mill effluents.
- Photocatalysis is generally employed for degradation of pollutants which are present in small amounts and are biorecalcitrant in nature.
- For a wastewater with organic loading that is not highly biodegradable, it is useful to apply integrated processes such as anaerobic process, photocatalytic treatment and another aerobic process in sequence.
- The effluents with relatively high biodegradable organics can be treated by integrated anaerobic-aerobic-photocatalytic-aerobic processes. Since, the cost being the major hurdle in the industrial applicability of photocatalytic processes, it is suggestive that photocatalytic treatment may be placed after the existing UASB-ASP-1 treatment for the enhanced degradation of recalcitrant contaminants present in effluents.
- The photocatalytic process efficiency was evaluated with catalyst (ZnO) in immobilized mode. Although the slurry mode achieved higher degradation as compared to immobilized mode, the latter is practically more feasible at industrial level.
- Instead of using multi-stage integrated AOP-biological systems, recycling of effluent in aerobic stage is another alternative for higher removal rate of contaminants. Recycling is helpful to keep the fixed cost lower than that of multi-stage processes. The circulation ratio is an important factor to determine the efficiency of the integrated AOP-biological method.

Intensification of AOPs with the existing biological treatment is one of the challenges of researchers in this area. Author is trying to develop more effective and economical treatment for pulp and paper mill effluents. Combining different

photocatalysts and irradiation sources are used to achieve higher synergetic effects for biodegradability enhancement. The future work in this direction may involve use of solar photocatalytic (immobilized mode) technology in tendem with existing biological treatment at pilot scale in order to improve its commercial viability. Approach will be helpful to determine the future direction of research and development in the area of environmental remediation with respect to pulp and paper industry.

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- Dhir A, Tejo Prakash N and Sud D (2012) Comparative studies on TiO_2/ ZnO photocatalyzed degradation of 4-chlorocatechol and bleach mill effluents. *Desalination and Water Treatment*, 46: 196-204.
- Dhir A, Tejo Prakash N and Sud D (2012) Coupling of solar assisted advanced oxidative and biological treatment for degradation of agro-residue based soda bleaching effluent. *Environmental Science and Pollution Research*, 19: 3906-3913
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- Bansal P, Dhir A, Tejo Prakash N and Sud D (2011) Environmental remediation of wastewater containing azo dye with a heterostructured nano photocatalyst *Indian Journal of Chemistry- Section A*, 50A, 991-995.