CHARACTERIZATION AND REMOVAL OF CHLORINATED ORGANICS FROM PULP BLEACHING EFFLUENTS

A THESIS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this thesis entitled **Characterization and Removal of Chlorinated Organics From Pulp Bleaching Effluents** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology, Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out at Department of Paper Technology during the period from January, 2007 to February, 2012 under the supervision of Dr. Satish Kumar, Professor & Head, and Dr. Nishi K. Bhardwaj, Assistant Professor, Department of Paper Technology, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

The growing environmental concern regarding the impact of bleach plant effluents has led to the progressive substitution of chlorine (Cl_2) based conventional pulp bleaching with environment friendly elemental chlorine free (ECF) and totally chlorine free (TCF) technologies for the regulation of chlorinated organic matter, AOX (adsorbable organic halides), in the effluents. The conventional effluent treatment processes are not effective for the degradation of chloroorganics and color removal from paper mill effluents. Hence, treatment with advanced oxidation processes (AOPs), e.g. photocatalysis, is needed which leads to the mineralisation of a wide range of organics without any harmful environmental impact.

The mixed hardwood kraft pulp was bleached to 87% ISO target brightness in the laboratory, for generating effluent, using D/CED, DED, DE_PD, and ODED sequences. The effluents generated were subjected to photocatalysis using UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes. The paper mill primary clarified (PC) and biotreated (BT) effluents were also subjected to photocatalysis using UV/TiO_2, $Solar/TiO_2$, $UV/TiO_2/H_2O_2$, and $Solar/TiO_2/H_2O_2$ processes. The catalyst characterization, recycling, treatment process efficiency, and economic feasibility studies were also performed. The effect of bleaching on the pulp viscosity and mechanical strength properties was also studied.

The bleach chemical consumption followed the order: DED > D/CED = DE_PD > ODED for attaining the same target brightness (87% ISO). O_2 pretreatment saved 45% bleach chemical (active chlorine), while DED sequence required 14% higher as compared to D/CED sequence. ECF bleaching sequences reduced alkali consumption by 30% as compared to D/CED sequence. The pulps obtained by ECF sequences were having slightly better properties as compared to D/CED sequences. O_2 pretreatment and H_2O_2 application in E stage reduced significantly the effluent pollution load.

Six types of chlorophenolic compounds, i.e. chlorophenols, chloroguaiacols, chlorocatechols, chlorovanillin, chlorosyringol, and chlorosyringaldehyde, were identified in the effluents. The generation of chloroorganics is highly reduced by ECF bleaching sequences. The chlorophenolics generation was reduced by about 93, 89, and 83% by ODED, DE_PD, and DED sequences, respectively, as compared to D/CED sequence. Four cRFA compounds, i.e.

chlorodehydroabietic acid, 12,14-dichlorodehydroabietic acid, 9,10-dichlorostearic acid, and 9,10,12,13-tetrachlorostearic acid were detected in the effluents. The generation of cRFA was reduced by about 82, 62, and 47% by ODED, DE$_P$D, and DED sequences, respectively, as compared to D/CED sequence. O_2 pretreatment, complete Cl_2 substitution by ClO_2, and H_2O_2 application in E stage was able to sharply decrease the generation of polychlorinated compounds.

DED, DE$_P$D, and ODED sequences were able to reduce AOX generation below Central Pollution Control Board (CPCB), India discharge standard (1 kg/t O.D. pulp). The pulp bleaching cost followed the order: DED > DE$_P$D > ODED > D/CED sequence. If AOX abatement at the source and end-of-pipe effluent treatment costs are considered, then the order is DED > D/CED > DE$_P$D > ODED sequence. Hence, the paper mills may look at ODED and DE$_P$D sequences to meet effluent AOX discharge standard. DE$_P$D sequence is an alternative for the mills where O_2 plant installation is not possible.

UV/TiO_2/H_2O_2 process was able to remove the higher amount of pollutants from pulp bleaching effluents as compared to UV/TiO_2 process. ODED sequence effluents were degraded to the highest extent followed by DE$_P$D, DED, and D/CED sequences. UV/TiO_2/H_2O_2 process was found more efficient followed by Solar/TiO_2/H_2O_2, UV/TiO_2, and Solar/TiO_2 processes for the remediation of paper mill effluents. Biotreated effluents were found to be more amenable to photocatalytic degradation as compared to primary clarified effluents. The biodegradability of the effluents improved substantially after photocatalysis by all the processes indicating easy removal of the pollutants by biological processes.

There was no significant loss in pollutants removal efficiency after reuse of TiO_2 for five subsequent effluent treatment cycles. The economical costs and environmental impacts of removing a certain quantity of COD from the effluent are very high when the processes use electric energy (UV/TiO_2 and UV/TiO_2/H_2O_2) as compared to those using solar light (Solar/TiO_2 and Solar/TiO_2/H_2O_2). Solar/TiO_2/H_2O_2 process was found the most economically viable followed by Solar/TiO_2 and UV/TiO_2/H_2O_2 processes. UV/TiO_2 process can not be used due to the highest treatment cost. On the basis of the pollutants removal efficiency and economic analysis, Solar/TiO_2/H_2O_2 process was found suitable for paper mill effluent treatment.

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ABBREVIATIONS

A_{HT}	Hot acid hydrolysis stage
AOPs	Advanced oxidation processes
AOX	Adsorbable organic halides
BOD	Biochemical oxygen demand
BT	Biotreated
C	Chlorination stage
CAGR	Compound annual growth rate
cb	Conduction band
CC	Chlorocatechols
CDAA	Chlorodehydroabietic acid
CED	Cupriethylenediamine
cFA	Chloro-fatty acids
CG	Chloroguaiacols
COD	Chemical oxygen demand
CP	Chlorophenols
cRA	Chloro-resin acids
cRFA	Chloro-resin and fatty acids
CS	Chlorosyringol
CSA	Chlorosyringaldehyde
CSF	Canadian standard freeness
CV	Chlorovanillin
D	Chlorine dioxide stage
D/C	ClO_2 followed by Cl_2 in combination
DCDAA	12,14-dichlorodehydroabietic acid
DCP	Dichlorophenols
DCSA	9,10-dichlorostearic acid
D_{HT}	High temperature ClO_2 stage
E	Alkaline extraction stage
ECF	Elemental chlorine free
EDX	Energy dispersive X-ray analysis
EE	Extraction efficiency
EI	Electron impact
EOX	Extractable organic halide
E_P, E_O, E_{OP}	H_2O_2 and O_2 reinforced extraction stages
FE-SEM	Field emission scanning electron microscope
FID	Flame ionization detector

FTIR	Fourier transform infrared
GC-MS	Gas chromatography-mass spectrophotometer
H	Hypochlorite stage
HexA	Hexenuronic acid
HMW	High molecular weight
IEP	Isoelectric point
KF	Kappa factor
LMW	Low molecular weight
m/z	Mass/charge ratio
MCP	Monochlorophenols
MTBE	Methyl tertiary butyl ether
O	Oxygen delignification stage
O.D.	Oven dried
P	Hydrogen peroxide stage
PC	Primary clarified
PCP	Pentachlorophenol
POPs	Persistent organic pollutants
RF	Response factor
RT	Retention time
S_{BET}	Brunauer-emmett-teller surface area
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCF	Totally chlorine free
TCP	Tri-chlorophenols
TCSA	9,10,12,13-tetrachlorostearic acid
Tet-CP	Tetra-chlorophenols
TOC	Total organic carbon
vb	Valence band
XRD	X – ray diffraction
Z	Ozone stage

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CHAPTER 1

INTRODUCTION

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1.1 PULP AND PAPER INDUSTRY

The worldwide paper and paperboard production (380 million tonnes in 2008) is dominated by North America, Europe, and Asia. Due to closing down of a large number of paper manufacturing capacities in North America and increasing capacity building in Asia (particularly China), the latter accounts for over a third of world's paper manufacture, followed by Europe (30%) and North America (25%). Paper demand is unequally dispersed as 22% of the world's population - in US, Europe, and Japan consume 72% of the global paper. The global demand is projected to grow by about 3% yearly, reaching an expected 490 million tonnes by 2020, with considerable increase coming out of Asia and Eastern Europe [1].

The Indian paper industry (Rs. 25,000 crore) accounts for about 1.6% of the global paper and paperboard manufacture. The Indian paper market size is increasing at a Compound Annual Growth Rate (CAGR) of 10.5% from Rs. 195/- billion (2003-04) to Rs. 321/- billion (2008-09). The industry is poised to grow from 9.18 million tonnes in 2009-10 to 11.5 million tonnes in 2011-12 at the rate of 8% per annum [2] and 15 million tonnes by 2015 [1]. The per capita paper consumption increased to 9.18 kg on 2009-10 as compared to 8.3 kg during 2008-09 with 10.6% growth. The figure is still low (9.2 kg) compared to China (42 kg) and developed countries (350 kg) [2]. The India's demand for paper is expected to double to 20 million tonnes by 2020 [3]. India has about 600 paper mills. The country's paper is mainly manufactured from hardwood and bamboo fibre (40%) followed by agro waste (30%) and recycled fibre (30%) [2]. The paperboard accounts for the highest fraction (47.3%) of the market size followed by writing and printing paper (29.6%), newsprint (19.5%), and speciality paper (3.6%) [1].

The paper manufacture consists of two major processes: pulping and bleaching. The pulping results in lignin network degradation and removal of its soluble fractions from the plant tissue producing unbleached pulp (cellulose 80-90%, hemicelluloses 10-15%, and residual lignin 2.5-4%). The residual lignin is accountable for the unwanted dark color and photo yellowing of the pulp [4]. The pulp bleaching is used to achieve the desirable pulp brightness and should be selective with regard to the lignin oxidation so as to preserve the pulp mechanical properties [5]. It is performed in a continuous sequence of different stages with in-between washing stages. The first stage is chlorination by chlorine (Cl_2) and/or chlorine dioxide (ClO_2) to delignify the pulp followed by an alkaline extraction (E) stage where alkali (NaOH) and oxygen (O_2) and/ or hydrogen peroxide (H_2O_2) are used for the removal of alkali soluble lignin. The following stages increase pulp brightness by removing chromophoric groups of lignin [6]. Indian paper mills are broadly grouped into three categories, i.e. large (> 100 tonnes per day), medium (30-100 tonnes per day), and small (< 30 tonnes per day) [7]. Large mills (wood and bamboo based) use chemical recovery while the smaller ones (agro based) with no chemical recovery are extremely polluting [8].

The mills in developed countries have reduced the pollution generation below the prescribed standards by switching over to modern technologies for pulping, bleaching, pulp washing etc. Indian mills have continued using Cl_2 for bleaching because of techno-economic reasons. CEH, CEHH or CE_PHH are the common bleaching sequences. Thus bleach plants have become a major source of environmental pollution releasing high biochemical oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halides (AOX), and color loads. Nowadays some of the Indian mills have shifted from conventional to elemental chlorine free (ECF) bleaching sequence like $DE_{OP}D$ to reduce the generation of chloroorganics. The mills are changing E stage to E_P/E_{OP} stage to reduce the effluent color. Some mills have started using small amount of ClO_2 in chlorination stage or applying ClO_2 as the last bleaching stage and O_2 delignification to reduce kappa number before bleaching.

1.2 PAPER INDUSTRY EFFLUENT CHARACTERISTICS

The paper industry comes under twelve most polluting industries in India due to the huge quantity and quality of the effluents generated [9]. Wood preparation, pulping, pulp washing, bleaching, and coating operations are the major sources of pollution. The effluents from pulp bleaching are responsible for most of the color, organic matter, and toxicity [10-12]. The paper industry effluent is characterized by high BOD (10-40 kg/t O.D. pulp), COD (20-200 kg/t O.D. pulp), suspended solids (10-50 kg/t O.D. pulp), AOX (0-4 kg/t O.D. pulp), color, toxicity, and high concentration of nutrients (phosphorus and nitrogen) which cause eutrophication in receiving water bodies [13]. Bleach plant discharges account for 60-70% of BOD and 80-90% of color load of the entire mill having chemical recovery [14].

The paper industry effluents are highly dark brown colored. First two pulp bleaching stages typically contribute over 90% of the total bleach plant effluent color and E stage individually 70-80% [15]. Color originates from thermal, mechanical, and chemical conversion of wood into pulp. These operations generate residual lignin and lignin derivatives, along with polymerized tannins in the effluent as by-products of lignin degradation, which are responsible for the effluent color. Color is also associated with wood extractives and chlorinated organics (e.g. phenols, dioxins, and furans etc.), formed during pulp bleaching [16, 17]. The pulp bleaching with Cl_2 and chlorine derived chemicals is known to generate various chlorinated organics (> 500) in the effluent, i.e. phenolics, chloro-resin and fatty acids (cRFA), dioxins and furans etc., which are collectively estimated as AOX [18, 19]. The chloroorganics generation is directly proportional to the consumption of Cl_2 or chlorine derived bleach chemicals [20]. Chloroorganics are toxins, biorecalcitrant, and tend to persist in nature, hence are known as persistent organic pollutants (POPs) [21]. They can be segregated in high molecular weight (HMW >1000 Dalton) and low molecular weight (LMW <1000 Dalton) fractions as defined by ultra filtration [22]. HMW fraction is the major contributor to COD, color, chronic toxicity, and total organic chlorine of the effluent. LMW fraction (acidic, phenolic, and neutral compounds) is the main contributor to BOD and acute toxicity of the effluent [23, 24].

1.3 TOXICITY OF BLEACHING EFFLUENTS

Effluent toxicity depends upon the total organically bound chlorine, extractive content of the raw material, and to what extent extractives are removed during different processes [25]. The high toxicity and low biodegradability of resins, long chain fatty acids, terpenes, tannins, lignins, and chlorinated compounds are mainly responsible for toxic effects of paper mill effluents [26]. The use of ECF and totally chlorine free (TCF) bleaching sequences involving replacement of Cl_2 by ClO_2 and/or H_2O_2, O_3, and enzymes reduce significantly the effluents toxicity [27]. HMW compounds (~80%) are biologically inactive due to inability to penetrate the cell membranes of the living organisms, while LMW compounds (~20%) are more problematic [28-29]. Out of 20% of LMW compounds, about 19% are hydrophilic and can be metabolized while 1% are extractable only by non polar solvents and are called as extractable organic halide (EOX). The compounds from this fraction bioaccumulate through food chain and are potentially toxic [28]. The chlorination (C) stage effluent toxicity is mainly caused by chlorophenolics (80% toxicity at a charge equivalent of 50% of chlorine demand) [30]. E stage effluent is responsible for 90% of acute toxicity. The chlorophenolics biodegradation rate decreases as the degree of chlorination increases [31]. E stage provides main toxic compounds that are found in the final process effluent [32]. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has been shown to be highly toxic, bioaccumulative, mutagenic, and carcinogenic. 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), pentachlorophenol (PCP), chlorinated furans, and chloroform are carcinogenic, where as chlorocatechols (CC) are strongly mutagenic [33].

The pulp and paper industry effluents affect reproductive physiology of fish through endocrine disruption [34]. They cause androgenic activity and result in masculinisation and sex-reversion of female fish [35]. The pulp mill effluents have been reported to induce mixed-function oxygenase enzymes in liver, reduction in gonad size, depression of circulating sex steroids, increase in plasma vitellogenin, and reduced ovarian development in fish under both laboratory and field conditions [36-40]. Resin acids have been reported to cause teratogenicity in fish larvae [41] and genotoxicity to mussels [42]. The hepatopancreas DNA activity decreased in mussels after exposure to abietic acid and dehydroabieteic acid [43, 44].

1.4 ORIGIN OF CHLOROORGANICS

Native lignin is a polymer comprised of p-coumaryl and coniferyl alcohols. The hardwood lignin is guaiacyl-syringyl lignin formed by copolymerization of coniferyl and sinapyl alcohols. 1-5% of p-coumaryl alcohol also participates in the formation of hardwood lignin [45]. Chlorophenolic compounds are generated as lignin degradation products during pulp bleaching using chlorination processes [31, 46]. The development of new analytical techniques such as Gas chromatography - Mass spectrophotometer (GC-MS) and capillary column of Gas chromatography have led to successful estimation of the chloroorganics in the effluents. The chloroorganics present in spent bleach liquor were first characterized by Lindstrom and Nordin in 1976 [47]. Huge amount of work has been reported for the identification of chloroorganics from softwoods [48], grasses [49-52], and agro-residues [53]. Few studies have been reported for the characterization of chloroorganics from Indian varieties of hardwoods [19, 54-57].

1.5 BLEACH PLANT POLLUTION ABATEMENT

The pollution abatement can be done either by in-plant technology modification or effluent treatment. In-plant technology modifications, i.e. extended delignification, O_2 delignification, improved pulp washing, xylanase pre-treatment, replacement of Cl_2 by ClO_2, oxidative alkaline extraction, ECF, and TCF bleaching reduce/ completely eliminate AOX generation and decrease bleach plant pollution load. The polluted effluent poses serious threat to the soil fertility and the life in the aquatic environment if discharged untreated [10]. The effluent treatment can further reduce or remove chlorinated organics and effluent pollution load.

1.6 IN-PLANT TECHNOLOGY MODIFICATIONS

1.6.1 Extended delignification

Extended delignification further decreases the pulp lignin content before the bleaching. The bleach chemical dose required to achieve certain pulp brightness is proportional to the residual lignin content (kappa number) of the pulp. Hence extended delignification can decrease the bleach chemical dose which in turn reduces the generation of chloroorganics during bleaching in proportion to lignin content reduction [58]. There are various extended delignification technologies to reduce kappa factor before pulp bleaching like - modified conventional batch cooking [59], rapid displacement heating [60], extended modified continuous cooking, and isothermal cooking [61]. These are based on the leveling out of the alkali profile throughout the cook, maintaining hydrogen sulfide concentration high in the initial phase and at the beginning of the delignification process, and the temperature as low as possible, especially in the beginning of the cook. An effective alkali profiling cook may lead to a pulp yield gain.

1.6.2 Oxygen delignification

The concerns about the release of paper mill effluents and recycling have forced the pulp and paper mills to lay more emphasis on chlorine free processes making oxygen (O_2) delignification an attractive pre-bleaching stage of current ECF and TCF bleaching processes [62]. O_2 delignification is being utilized by almost all the pulp mills in the developed nations to further decrease unbleached pulp kappa number before bleaching. This process decreases the kappa number by 40-50%, chlorine utilization by 50-60%, and AOX generation by 60-70%

[63]. A delignification higher than 50% leads to oxidative degradation of polysaccharides and deterioration of pulp quality [64].

During the recent years efforts have been made to increase the efficiency of O_2 delignification, e.g. reinforcement with peroxide or peracids, activators or catalysts addition, pulp pre-treatment before O_2 delignification, and two-stage O_2 delignification (OO) with or without inter stage treatment [65-67]. O_2 delignification is superior in selectivity relative to kraft pulping. The pulp yield can be enhanced by terminating the kraft cook at a higher than normal kappa number and using the more selective O_2 stage to complete the delignification to kappa numbers at which other bleach chemicals can take over [68]. The O_2 delignification results in considerable decrease in the effluent pollution load [69], power, water consumption, and effluent generation [70]. The partial closure of fiber line is possible by recycle of O_2 stage effluent to chemical recovery [71]. The tangible profit consists of savings by decreased chemicals consumption for pulping and bleaching [58, 72].

1.6.3 Improved pulp washing

The aim of pulp washing is to remove as much of the soluble impurities as possible from pulp using a small amount of fresh water [73]. The modern eucalyptus kraft pulp bleach plants equipped with state-of-the-art washing equipment produce pulp for bleaching with COD as low as 5 kg/t O.D. pulp., while, poor washing of brown stock, and post-oxygen washing in older mills result in COD (20-30 kg/t O.D. pulp) and resin carry over along with pulp to bleach plant [65]. These substances compete with the remaining lignin in the pulp for reaction with the bleaching chemicals and lead to high chlorine consumption and eventually high AOX generation [58, 74]. The active chlorine consumption increases approximately 0.085% for every unit of COD carried over with O_2 delignified pulp [65]. About 10-20% of AOX is generated due to solids carry over during good washing while 25-40% during poor washing. These solids consume 10-25% of the active chemical charge applied in first bleaching stage [75]. Poor pulp washing also leads to generation of higher dioxin type compounds [76]. Thus improved washing can decrease the requisite bleach dose, cost, and the consequent decrease in chlorinated organics in addition to conventional pollutants [58]. $DE_{OP}DP$ sequence (washing) required less chlorine dioxide dose than normal $DE_{OP}DP$ sequence, resulting in about 4% chemical costs reduction [77]. Good washing combined with decreased consumption of fresh water and thus reduced effluent generation reduces bleach plant environmental impact, size of effluent treatment plant, and cost [78].

1.6.4 Enzyme pretreatment of pulp

Lignin removal by biological means is known as bio-bleaching. The inclusion of enzymes as an alternative to chlorine based chemicals for pulp bleaching is simple, cost-effective, and eco-friendly [79]. Xylanase [80] and lacasse [81] enzymes, from different origin, have been investigated as potential agents for bio-bleaching of kraft pulp. Xylanases hydrolyze xylan layer present in the plant cell wall and influence the structural integrity and this facilitate lignin removal during succeeding bleaching stages. Simultaneously, xylanases also act on xylan which re-precipitates on the pulp fibers surface during chemical pulping and thus boost bleaching by exposing lignin to the action of bleaching chemicals [82, 83]. Lacasses directly and specially act on lignin, oxidize, and make it water soluble. Lacasses attack primarily the phenolic groups by simultaneous reduction of O_2 to H_2O_2 through phenoxy radicals formation as intermediate [84]. Xylanase application can decrease pulp hexenuronic acid (HexA) content which adversely affects pulp bleachability by increasing chemical consumption [85]. Singh et al. [80] reported the reduction in kappa number (24-28%) and AOX (55-68%) generation during bio-bleaching of wheat straw pulp with xylanases from *Coprinellus disseminatus*. Garg et al. [86] reported 20% reduction in chlorine consumption, 7.1% decrease in kappa number, and brightness improvement by 4.8% after enzymatic pre-bleaching with xylanases produced from *Bacillus stearothermophilus*.

1.6.5 Chlorination (C) stage modifications

The pulp bleaching with Cl_2 results in the generation of toxic compounds in the effluent [19]. Slow, multipoint, and continuous addition of Cl_2 bleach liquor at either 3.5 or 10% pulp consistency, increases viscosity of pulp and reduces AOX generation in the effluent [87]. The replacement of ClO_2 for elemental Cl_2 as a bleaching agent is gaining extensive application owing to its beneficial impacts on pulp and effluent quality [58]. ClO_2 addition (3 kg/t O.D. pulp) in C stage in addition to Cl_2 improves pulp brightness (4 points) and viscosity as well as decreases Cl_2 dose (15 kg/t O.D. pulp) and effluent COD (10%) [73]. ClO_2 has five times higher oxidation power as compared to Cl_2 and it reacts mainly by addition reactions with aromatic lignin compounds [88]. One weight unit of ClO_2 can replace 2.63 weight units of Cl_2 [4]. The proportion of oxidative reactions increases by application of ClO_2 instead of Cl_2. This results in decreased generation of chloroorganics in the effluent. ClO_2 bleaching generates about 20% of the chloroorganics as generated by applying Cl_2 and most importantly the generation of highly substituted chlorinated toxic compounds is reduced [58]. Jain and Carpenter [89] reported significant reduction in effluent BOD (20-30%) and color (50-80%) at high to complete substitution of Cl_2 by ClO_2 (90-100%). AOX and chlorophenolics generation in the effluent decrease by 70-80 and 95%, respectively, at 100% of ClO_2 substitution for Cl_2 [90].

1.6.6 ECF bleaching

ECF bleaching is presently the dominant technology in the high brightness market chemical pulp production. About 75% of the world's bleached chemical pulp is manufactured by ECF technology [91-93]. ClO_2 has been utilized as a promising delignifying reagent for pulp bleaching owing to its high selectivity, i.e. preferentially oxidizing lignin in the presence of carbohydrates thus preserving pulp quality, and significant decrease in generation of AOX [94, 95]. High temperature ClO_2 pre-bleaching (D_{HT}, 120 min/95 °C) gave better efficiency as compared to conventional D_O (30 min/60 °C) stage with respect to D_OE kappa decrease and final brightness achievement [91]. About 40-50% less AOX is generated with D_{HT} stage as compared to conventional D_O stage at constant charge. The higher reaction time/temperature in D_{HT} stage not only produces fewer chlorinated compounds but also decomposes them [91, 96]. Mellander et al. [97] reported decrease in total ClO_2 consumption (42%) with hot acid treatment (A_{HT}) in $A_{HT}(DZ)E_{OP}D$ sequence as compared to $D_OE_{OP}D$ sequence. $A_{HT}Z_{HC}DP$ sequence presented lower operating cost at 91% ISO brightness level along with partial bleach plant closure and consequently lower environmental impact [77]. D_{HT} stage reduces HexA content and improves the pulp brightness and optical properties as compared to D_O stage [98]. The combined use of O_3 and ClO_2 (D/Z or Z/D) in an ECF sequence has several benefits, i.e. chemical savings, efficient kappa reduction, brightness development in preceding stages, and decrease in chloroorganics generation at the same time preserving strength of bleached pulp [99, 100]. The filtrates from first two bleaching stages of OZ/EDP, OZ/E_PDP, $A_{HT}E_{OP}DP$, Z/E_ODD, and Z/E_ODP sequences can be recycled to recovery section and this minimizes the effluent volume to be treated [68].

1.6.7 H_2O_2 reinforced alkaline extraction

H_2O_2, as an O_2 based chemical, has found an important role in ECF and TCF bleaching sequences for chemical pulps in addition to the mechanical pulp bleaching [61,101]. H_2O_2 has been applied as a primary chemical of a bleaching stage as well as a reinforcer for E stage [102]. The use of E_P stage is growing significantly for bleaching processes that requires only 0.3-0.5% H_2O_2 [68]. E_P stage increases delignification and pulp brightness while decreases active chlorine requirement in the subsequent bleaching stages, cost, and the effluent pollution load [58, 103]. Sharma et al. [104] reported decrease in BOD, COD, and color (10-20%) of bleach plant effluent from an agro-based mill with oxidative extraction. E_{OP} stage reduced CE kappa (33%), COD (15%), color (35%), and improved pulp brightness [73]. The quantity of ClO_2 that can be replaced by H_2O_2 application in E stage varies from 0.6 to 2.5 (wt. ClO_2/wt. H_2O_2) [105]. The E_{OP} stage filtrate can be recycled for post oxygen washing thus further reduce the pollution load [106].

1.6.8 TCF bleaching

The need for reducing the environmental impact of pulp mills gave a more prominent role to oxygen-based bleaching reagents such as O_2, H_2O_2, and O_3 in TCF bleaching technology [107]. O_3 is an extremely efficient oxidant and is able to oxidize all types of lignin structures [108]. O_3 bleaching can potentially eliminate the need of chlorine for pulp bleaching and is carried out with processes and equipment similar to that of O_2 stage [58]. The medium consistency O_3 bleaching is a primary choice for ensuring an efficient and selective O_3 bleaching [99]. Extended or O_2 delignification are considered a prerequisite for good O_3 bleaching. The combined application of O_2 and O_3 can result in a high quality brightness pulp which needs little or no Cl_2 or ClO_2 bleaching [58]. O_3, as a potential alternative to Cl_2 and ClO_2, reduces AOX generation without significantly affecting the operating cost of bleaching [109]. O_3 bleaching significantly decreases pulp HexA content [110]. H_2O_2 plays an important role in TCF advanced bleaching sequences for achieving high brightness within the minimum impact mill concept. The pulp bleaching with a final peroxide stage have low brightness reversion and better strength properties as compared to D_2 stage pulp [107].

1.7 EFFLUENT TREATMENT

The conventional, primary clarification and biological, remediation processes utilized by Indian paper industry for effluent treatment suffer from low efficiency for chlorinated organics removal and no color decrease [111, 112]. With increasingly stringent effluent discharge standards and growing environmental awareness, there is a need to adopt technologically advanced treatment systems such as advanced oxidation processes (AOPs). AOPs rely on the in-situ generation of very reactive and non-selective oxidizing species i.e. hydroxyl radicals ($OH^{\bullet}$) for the degradation of organic compounds [113, 114]. $OH^{\bullet}$ radicals are reactive electrophiles (2.33 V oxidation potential), hence cause rapid degradation of nearly all electron rich organic compounds [115].

For the effective oxidation of organics, $OH^{\bullet}$ radicals must be generated continuously through chemical or photochemical reactions. Their generation can be accelerated by combining various systems, i.e. Fe(II)/Fe(III) with H_2O_2 (Fenton reaction) [116], UV/{Fe(II)/Fe(III)+H_2O_2}(photo-Fenton) [117], UV/H_2O_2, UV/O_3, O_3/H_2O_2, UV/O_3/H_2O_2 [118-120], UV/catalyst and UV/catalyst/H_2O_2 (photocatalysis) [121]. Depending on the quality of effluent AOPs can be applied independently or as a pre or post-treatment remediation step for enhancing degradability of pollutants. High electrical energy input and chemicals consumption are the common problems hindering their industrial application. However, several AOPs can be performed under solar irradiation which is a cleaner and renewable energy resource [122]. Among the various AOPs discussed above, the photocatalysis utilizing TiO_2 or ZnO with UV/solar radiation is very efficient for environmental remediation [123].

1.7.1 Photocatalysis

The photocatalysis is an emerging technique for the remediation of both aquatic and atmospheric pollutants [124-127]. The photocatalyst leads to the complete mineralization of organic pollutants essentially to CO_2, H_2O, NO_3^-, PO_4^{3-}, and halide ions [128]. Various catalysts (TiO_2, ZnO, MgO, WO_3, Fe_2O_3, CdS, and ZnS) are being explored for photocatalysis. Among them, TiO_2 is the most widely used photocatalyst because it is chemically and biologically inert, photostable, non-toxic, low cost, and relatively easy to produce and use [114, 124, 129]. TiO_2 is photochemically more stable in aqueous media as compared to ZnO [130]. TiO_2 band-gap energy (anatase: 3.2 eV; rutile: 3.03 eV) is comparatively smaller as compared to

ZnO (3.35 eV) and SnO_2 (3.6 eV) semiconductors [131]. Hence, it is capable of absorbing photons energy in the near UV region (< 387 nm) [129]. The sun produces 0.2-0.3 M photons $m^{-2}h^{-1}$ (300-400 nm) with a characteristic UV flux of 20-30 Wm^{-2} near the Earth's surface. Thus sunlight can be utilized as an economical and ecologically sensible source of light [132].

Fujishima and Honda in 1972 were the first to discover ability of TiO_2 in splitting water in the presence of UV light [133]. Frank and Bard [134] were the first to examine the possibilities of using TiO_2 to decompose cyanide in water. TiO_2 exists in five different forms in nature, i.e. anatase, rutile, brookite, monoclinic, and orthorhombic [129]. Anatase is mainly used as a photocatalyst under UV irradiation for environmental remediation. It is the most stable form and has higher photocatalytic activity than rutile due to the difference in their chemical properties, crystal, and electronic structure. But the best photodegradation efficiency is obtained when a mixture of anatase and rutile is used because the rutile phase introduces mesoporosity and a wider pore size distribution [114, 135].

1.7.2 Mechanism of treatment

The exposure of TiO_2 to UV radiation leads to the excitement of electrons from the valence band to the conduction band leaving behind highly oxidative holes in valence band and generation of radicals (mainly $OH^{\bullet}$). Pollutants are oxidized by holes on TiO_2 surface as well as by radicals in the solution [136, 137]. The photocatalytic oxidation of pollutants depends on various parameters, i.e. catalyst type (composition, concentration, particle size, and calcination temperature), pollutant type and concentration, light wavelength and intensity, ionic composition of effluent, pH, and oxidant concentration [138-141]. The hydroxylation of aromatic compounds by $OH^{\bullet}$ radicals lead to consecutive oxidation/ addition and ultimately ring opening. The intermediates generated, mainly aldehydes and carboxylic acids, will be further carboxylated to form harmless CO_2 and H_2O_2 [142].

1.7.3 Reactor configurations

Photocatalysis for water treatment can be carried out in two types of reactors depending on the state of the catalyst: (1) catalyst particles suspended in solution and (2) catalyst immobilised onto an inert support, i.e. activated carbon, mesoporous clays, fibers, and membrane [142-146]. The slurry reactors are more preferred owing to high surface area of catalyst per unit volume available for adsorption of pollutants. They allow more number of photons to hit the catalyst and are easier to make and maintain. The immobilised systems suffer from mass transfer limitation, catalyst fouling, and deactivation [135, 142]. The slurry reactors require a post-treatment separation of catalyst particles which is usually carried out using coagulation and centrifugation [114], sedimentation [147], cross-flow filtration [148], and membrane filtration [149]. Malato et al. [150] carried out induced coagulation by pH control close to the isoelectric point for TiO_2 separation. The microfiltration recovered the remaining 3% catalyst particles.

Different reactor configurations utilized for the photocatalytic water treatment are annular [151], immersion well [152], elliptical, multi-lamp, film type, and fluidized bed [153, 154]. Different solar reactors used are: parabolic trough reactor, compound parabolic collecting reactor, double skin sheet reactor, and thin film fixed bed reactor [155, 156]. Application of photocatalytic membrane reactors, i.e. microfiltration [157], ultrafiltration [158], and nanofiltration [159], prevents use of coagulation, flocculation, or sedimentation to recover the catalyst from the treated water. The photocatalytic reaction occurs either on membrane surface or within its pores [142].

1.7.4 Photocatalysis and biological hybrid system

Chemical oxidation of pollutants for complete mineralization is usually costly because the intermediates produced have a tendency to be more and more resistant to their total degradation. Additionally, the consumption of energy and chemical reagents increases with treatment time [122]. The application of the chemical oxidation process as pre-treatment to change persistent pollutants into more biodegradable intermediates is an attractive alternative. The biodegradable products would then be treated in a biological oxidation process with a significantly lower cost [160]. The more biodegradable organics are readily utilized as substrates by microorganisms [161]. By this, the reaction volume and residence time for the biological treatment could be considerably decreased. But the degree of mineralization should be minimal after pre-treatment so as to avoid unnecessary consumption of reagents and energy [142]. A chemically over oxidized effluent having the highly degraded products is of minimal value for the microbes [162]. If the pre-treatment time is too small, the intermediates formed could still be structurally very similar to the original persistent components [142]. If the effluent contains a significant quantity of biodegradable organics, the pre-oxidation will not lead to a considerable improvement in the biodegradability rather it will lead to needless expenditure of chemicals. Here, a biological pre-treatment, removing biodegradable organics, followed by an oxidation step, converting persistent fraction into biodegradable compounds with a smaller amount of chemical, and a final biological polishing step may prove to be more beneficial [163, 164].

1.7.5 Improvement in the activity of TiO_2

The Sun light is an environmentally friendly, cheaper, and inexhaustible source of energy [150]. TiO_2 shows its photoactivity only under UV light. The comparatively wide band-gap of TiO_2 (3.2 eV) indicates that it can be stimulated only by UV light with about 387 nm wavelength. Consequently, only about 3-5% of received solar radiation on the Earth's surface can be used and is hence impractical for effluent treatment [165, 166]. The doping of pure TiO_2 with foreign ions can sensitize TiO_2 to visible light and also form charge traps to keep e^-/h^+ pairs separate [167]. The photocatalytic degradation of pollutants under solar light has been made feasible by doping TiO_2 with transition metals, e.g. cobalt (Co) [168] and iron (Fe) [169], non-metallic elements [170], or noble-metals, e.g. silver (Ag) [171] and platinum (Pt) [172]. The doping could widen the light absorption range, improve the redox potential of the photogenerated radicals, and enhance quantum efficiency through preventing the recombination of photogenerated e^- and h^+ and the ions act as e^- traps [129]. The surface chlorination of TiO_2 based catalysts has been reported to improve significantly the photocatalytic activity [173].

1.7.6 Literature review of photocatalytic treatment of paper industry effluent

TiO_2 photocatalysis has been successfully utilized for the treatment of pulp and paper industry effluents either singly or in combination with other chemical, physicochemical/ or biological processes with promising results. A review of the work done during the last years in the area of photocatalytic paper industry effluents treatment is presented in Table (1.1).

Perez et al. [174] reported that photocatalysis can efficiently reduce the organic load from ECF bleaching effluent. Mansilla et al. [175] observed that photocatalysis ($UV/ZnO/O_2$ and $UV/TiO_2/O_2$) is more effective than homogeneous systems (O_3) for the degradation of phenolic and polyphenolic compounds from pulp bleaching effluent. Zamora et al. [176] studied that TiO_2 was more efficient than ZnO and both were better than immobilized ZnO for the photodegradation of cellulose and textile industry effluents. Balcioglu and Arslan [177] investigated that UV/TiO_2/H_2O_2 process was more efficient for the removal of pollutants from pretreated textile and pulp effluents. Treatment efficiency depended upon extent/ type of pretreatment and initial COD of the effluents. Langford et al. [178] reported complete photocatalytic degradation of both dissolved and colloidal organic matter in paper mill white waters. UV/TiO_2/H_2O_2 process was more effective than UV/TiO_2 and UV/H_2O_2 processes. Balcioglu and Cecen [179] observed increase in biodegradability during photocatalysis of sulphate pulp bleaching effluent (raw and bio-treated). The process efficiency strongly depended on initial chloride and COD concentration in the effluent. Wang [180] reported that UV/H_2O_2 process is better than UV/TiO_2 process for the photo-degradation of paper mill effluent. Synergistic effect was observed when H_2O_2 and TiO_2 were used together. Yeber et al. [181] investigated that supported and suspended systems were equally efficient for the degradation of bleaching effluent but with different reaction times.

Yeber et al. [182] reported reduction in total organic carbon (TOC) and significant improvement in biodegradability of ECF bleaching effluent after small period of treatment. The acute toxicity removal was most evident with TiO_2. Yeber et al. [183] reported that supported TiO_2 is better than ZnO for the degradation of organic compounds present in bleaching effluent. The acute toxicity and AOX were strongly reduced and HMW compounds were almost completely degraded after photocatalytic oxidation. Similarly, Perez et al. [184] reported that photocatalysis is efficient for the removal of AOX, TOC, total phenols, and toxicity from ECF bleaching effluent. The pH and catalyst load were main factors affecting AOX and COD removal. Mattos and da Silva [185] observed that UV/ZnO/O_2 process was better than UV/TiO_2/O_2 process for the degradation of ECF bleaching effluent. Balcioglu et al. [186] reported improvement in BOD/COD ratio of Kraft bleaching effluent after the photocatalysis. The treatment efficiency of AOP depended upon the type of pre-treatment, initial organic load of effluent, and nature of pollutants. Ksibi et al. [187] studied the photocatalytic degradation of lignin black liquor. The degradation compounds (vanillin and vanillic acid) could be isolated and used as valuable industrial products. Machado et al. [188] investigated that Degussa P25 is a better photocatalyst than anatase form of TiO_2 for photodegradation of paper mill effluent. The addition of H_2O_2 increased the efficiency of photodegradation. Boyd and Almquist [189] observed that photocatalysis with TiO_2 is an effective method for the degradation of COD and toxicity from pulp and paper mill effluents with initial COD concentrations of 500 mg/L or less. Effectiveness of photocatalysis was dependent on initial concentration of pollutants in the effluent and treated effluent can be recycled for system closure. Peralta-Zamora et al. [190] reported that COD degradation reaction is first order and significant removal was achieved after 2 h of treatment. Sattler et al. [191] achieved promising results in the solar photocatalytic treatment of paper mill effluents especially with compound parabolic collector type solar reactor. Amat et al. [192] reported that during the solar degradation of real effluent in board paper industries the best performance was obtained in closed circuits when COD values were higher. Closed circuits lead to accumulation of phenols and their easy degradation.

Munoz et al. [122] carried out life cycle assessment for different AOPs and observed that UV/TiO_2 and photo-Fenton processes were having the lowest environmental impact because these processes do not consume simultaneously both TiO_2 and H_2O_2, the chemicals with the highest environmental impact. Similarly, Munoz et al. [193] observed that the combined treatment i.e. UV/TiO_2 process followed by Fentons reagent has lowest environmental impact while UV/TiO_2 process is the worst AOP for the removal of dissolved organic carbon content from kraft bleaching effluent. Pedroza et al. [194] investigated that sequential, biological and photocatalytic treatment resulted in about complete degradation of bleaching effluent in terms of COD, color, and chlorophenols. Yeber et al. [195] used Cu (II) as an electron acceptor for the photocatalytic oxidation of kraft bleaching effluent and obtained promising results in terms of color, COD, BOD, and ecotoxicity reduction. Residual Cu (II) (0.05 mg/L) was not toxic to the next biological stage. Yuan et al. [196] studied photodegradation of paper mill effluent with TiO_2 loaded on activated carbon fibers. Supported catalyst showed better results than suspended form of catalyst. Toor et al. [197] reported that the rate of degradation of bleach plant effluent increases with increase in UV intensity, increase in aperture to volume ratio, and decrease in initial COD concentration. Kansal et al. [10] observed that TiO_2 is a better photocatalyst for acidic while ZnO for basic bleaching effluents. Treatment under solar light showed comparable results. Boroski et al. [198] reported that electrocoagulation-flotation followed by photocatalysis can efficiently reduce organic and inorganic contaminants from the pulp bleaching effluent.

Rodrigues et al. [199] reported similar findings during coagulation-flocculation followed by heterogeneous photocatalysis of bleaching effluent. $UV/TiO_2/H_2O_2$ process was found more efficient. Catalkaya and Kargi [123] reported that UV/TiO_2 system under alkaline conditions removed the highest toxicity and TOC from paper mill effluent as compared with other AOPs. Ugurlu and Karaoglu [200] investigated that during photodegradation of paper mill effluent AOX, total nitrogen, and lignin concentration go through a minimum when the concentration of H_2O_2 and TiO_2 increases at constant pH and UV intensity. The degradation rate for $UV/TiO_2/H_2O_2$ process was higher than by UV/H_2O_2 process. Shivaraju et al. [201] investigated photocatalytic oxidation of pollutants present in the paper mill effluent by supported photocatalyst. Easy recovery and reuse of recovered catalyst were the major advantages. The recycled catalyst showed acceptable level of treatment efficiency. Silva et al. [202] studied treatment of organic material from bleached pulp mill effluent by UV/H_2O_2 and $UV/TiO_2/H_2O_2$ processes. The photocatalysis coupled with H_2O_2 is reported to be more meritorious. Dhir et al. [203] reported that coupled system i.e. biological treatment followed by photocatalysis is an efficient method for the removal of TOC and COD from the paper mill effluent. Ghaly et al. [204] reported that solar photocatalysis using prepared TiO_2 is effective for COD removal from the paper mill effluent. The degradation was strongly enhanced in the presence of H_2O_2. The bio-recalcitrant matter can be effectively oxidized by the solar photocatalysis. Parilti and Akten [205] studied solar degradation of pulp mill effluents using TiO_2/Fe(III). Fe(III) and TiO_2 concentrations were the important parameters for color, TOC, and AOX removal. Thongkrua and Ratanatamskul [206, 207] reported supervibration-photocatalytic reactor as an effective technique for the degradation of lignin and 2,4-DCP.

1.8 STATEMENT OF THE PROBLEM

Water pollution is a major concern for the pulp and paper industry due to the large quantity and toxicity of the effluents generated. The effluents from pulp bleaching are responsible for most of the color, organic matter, and toxicity [10]. The pulp produced by chemical pulping requires bleaching to produce bright pulps. The use of chlorine and chlorine based chemicals for pulp bleaching generates a variety of chloroorganics in the bleach plant effluent originating from chlorination of residual lignin [19, 200, 208]. These chloroorganics are collectively estimated as AOX [49, 54]. Studies indicate that some of the chloroorganics are toxic, mutagenic, and resistant to biodegradation [20, 27]. Chlorophenolics, chloro-resin, and fatty acids (cRFA) present in the paper mill effluents are reported to be the most toxic to aquatic organisms [209, 210]. The bleach plant pollution abatement can be done by adopting the following two approaches:

(1) In-plant technology modification for reducing generation of AOX.

(2) Treatment of generated effluent for further reducing pollution load.

O_2 delignification, ClO_2 replacement for Cl_2, and the application of H_2O_2 in first alkaline extraction stage (E_P) reduce generation of chloroorganics [4, 211, 212].

The conventional biological effluent treatment processes are not efficient for the degradation of many of the chloroorganics with no color removal. Hence, treatment with advanced oxidation processes (AOPs) is needed [213]. AOPs rely on the in-situ generation of very reactive hydroxyl radicals ($OH^{\bullet}$) for the degradation of pollutants [113, 114]. TiO_2 photocatalysis, an AOP, has emerged as a promising technology for the partial or complete mineralisation of a wide range of pollutants from waste streams including chloroorganics [142, 214, 215]. TiO_2 as a photocatalyst has been successfully utilised, at laboratory scale, for the remediation of pulp and paper mill effluent during the recent years [123, 161, 199, 200].

The aim of this work is to characterize the chlorinated organics during chemical pulp bleaching, to reduce the generation of pollutants in the effluent by pulp bleaching technology modification, and their subsequent removal by effluent treatment with TiO_2 photocatalysis. The bleaching modifications studied were - replacement of C by D, reinforced alkaline extraction, and use of oxygen delignification. The mixed hard wood pulp was bleached in the laboratory for generating effluent and the photocatalytic treatment was carried out under UV irradiation. The photocatalytic treatment using UV and solar irradiation was also carried out for paper mill effluents. The following objectives were formulated for this study:

1. To bleach the pulp to 87% ISO target brightness using D/CED, DED, DE$_P$D, and ODED sequences. The kappa factor was varied to achieve the target brightness.
2. To compare D/CED, DED, DE$_P$D, and ODED sequences with regard to:
    - Bleach chemical consumption
    - Pollution load generation: by characterizing the effluents generated in terms of BOD, COD, color, AOX, chlorophenolics, cRFA
    - Pulp viscosity and mechanical strength properties of paper produced
    - Bleach chemical costs
3. To optimize the treatment conditions (catalyst dose, pH, time, oxidant concentration, light intensity, and temperature) for TiO_2 photocatalysis and to treat both the laboratory generated bleaching effluents and paper mill (primary clarified and biotreated) effluents under optimized treatment conditions using UV/TiO_2/H_2O_2, UV/TiO_2, Solar/TiO_2/H_2O_2, and Solar/TiO_2 processes for studying environmental load reduction.
4. To study catalyst recycling and economic feasibility of the treatment process.

Table 1.1 Literature review of photocatalytic treatment of paper industry effluent

Lamp	Effluent	AOPs studied	Remarks	Reference
125W	Bleaching (D)	$UV/TiO_2/O_2$	80% AOX, 64% COD, & 72% color removed	[174]
125W	Bleaching (E_{OP})	O_3, UV/O_3, $UV/TiO_2/O_2$, $UV/ZnO/O_2$, & $UV/ZnO/O_3$	40% color & 50% COD removed in first minute of treatment by heterogeneous systems	[195]
250W	E_1, bleach liquor, bleaching mixture, final effluent & textile	$UV/TiO_2/O_2$, $UV/ZnO/O_2$, & $UV/ZnO/O_2$ (silica gel supported)	50% mineralization & 50% toxicity removed, free form more effective than supported	[176]
20W	Coagulated & bitreated CEH, DED, combined (CEH+DED), textile, & dye	$UV/TiO_2/H_2O_2$	43-87% COD removed for biotreated & 20-38% for raw effluent	[177]
40W/ 16 (75W)	Synthetic & real pulp mill white water	UV/TiO_2, UV/H_2O_2, & $UV/TiO_2/H_2O_2$ (Supported & free TiO_2)	Non-polar organics decreased, polar organics increased, $UV/TiO_2/H_2O_2$ more effective	[178]
20W	Sulfate pulp bleaching (mixed raw, CEH, DED, & biotreated)	$UV/TiO_2/H_2O_2$	BOD/COD ratio improved	[179]
40W	Bleaching (C, E, D/C, & OE_1)	UV/TiO_2, UV/H_2O_2, & $UV/TiO_2/H_2O_2$	60% AOX, COD, & color removed, $UV/TiO_2/H_2O_2$ more effective	[180]
125W	Bleaching (DE_{OP} & CE_{OP})	$UV/TiO_2/O_2$ & $UV/ZnO/O_2$ (suspended/ supported)	Biodegradability increased, acute toxicity reduced	[181]
125W	Bleaching (E_{OP})	O_3, UV/O_3, $UV/ZnO/O_3$, $UV/TiO_2/O_3$, $UV/ZnO/O_2$, & $UV/TiO_2/O_2$	All AOPs rapidly removed COD, especially in photocatalyzed systems, biodegradability increased	[182]
125W	Bleaching (E_{OP})	$UV/TiO_2/O_2$ & $UV/ZnO/O_2$ (supported)	Effluent completely decolorized, total phenols (85%), TOC (50%), & AOX highly reduced after 120 min by both catalysts, TiO_2 better than ZnO	[183]

Table 1.1 *Continued*

Lamp	Effluent	AOPs studied	Remarks	Reference
125W	Bleaching (E_{OP})	UV/TiO_2 & UV/TiO_2/H_2O_2	After 30 min >60% toxicity removed, after 420 min no chloroorganics detected, 95% AOX, & 50% TOC removed	[184]
250W	$DE_{OP}D_1E_2D_2$	UV/TiO_2/O_2 & UV/ZnO/O_2	After 480 min color reduced by 69.4 & 57.0% while phenols by 57 & 37% with UV/ZnO/O_2 & UV/TiO_2/O_2, respectively.	[185]
125W	Raw, biotreated, & coagulated Kraft bleaching	UV/TiO_2/H_2O_2	Efficiency depends on type of pre-treatment and initial organic load, BOD/COD improved	[186]
125W	Black liquor	UV/TiO_2	Lignin successfully decolorized and degraded	[187]
400W/ sunlight	Paper and cellulose mill	Solar/TiO_2, UV/TiO_2, & UV/TiO_2/H_2O_2	P25 gave 60% higher degradation rate than anatase. H_2O_2 with P25 increased efficiency by 173.5%. >80% organic matter mineralized after 60 min, solar treatment showed excellent results	[188]
450W	Paper mill (primary clarified)	UV/TiO_2/O_2	90% COD & acute toxicity removed	[189]
125W	Paper mill	UV/TiO_2/H_2O_2	80% COD removed after 2 h	[190]
125, 400 , 1KW/ sunlight	Paper mill	UV/TiO_2	Very fast and total mineralization of non-biodegradable contaminants	[191]
300W/ sunlight	Cardboard paper	Photo-Fenton & UV/TiO_2	BOD increased by 30-50%	[191]
6W	Bleaching (D_{20}/C_{80})	UV/TiO_2, UV/TiO_2/H_2O_2, UV/TiO_2+Fenton, & photo-Fenton.	Solar energy reduced environmental impact by >90% for all AOP's, UV/TiO_2 & photo-Fenton better	[192]
6W	Bleaching (D_{20}/C_{80})	UV/TiO_2,UV/TiO_2/H_2O_2, UV/TiO_2+Fenton, photo-Fenton, O_3, & O_3/UV	UV/TiO_2+Fenton have lowest environmental impact	[193]
----	Bleaching	UV, UV/TiO_2, UV/TiO_2/Ru_xSe_y, (film) & biological by UV/TiO_2/Ru_xSe_y (film)	92% color, 97% COD, & 99% chlorophenols removed by combined treatment	[194]
120W	Bleaching (E_{OP})	UV/TiO_2/Cu(II) & UV/TiO_2/O_2	94% color, 70% COD, & 50% TOC removed, biodegradation increased from 0.3 to 0.6, ecotoxicity reduced	[195]

Table 1.1 *Continued*

Lamp	Effluent	AOPs studied	Remarks	Reference
500W	Mill effluent	UV/TiO_2/ACF & UV/TiO_2	High COD removed by TiO_2/ACF in short period, more effective than UV/TiO_2	[196]
8 (40W)/ sunlight	Bleaching	UV/TiO_2	86.6% COD removed after 4 h	[197]
5 (30W)/ sunlight	Bleaching (C & E)	UV/TiO_2 & UV/ZnO	COD and BOD reduced	[10]
3 (250W)	O_3 Bleaching	Electrocoagulation–flotation followed by UV/TiO_2/H_2O_2	88% COD reduced, biodegradability increased from 0.15 to 0.89	[198]
250W	Bleaching	Coagulation-flocculation followed by UV/TiO_2/H_2O_2, UV/TiO_2, UV/H_2O_2, & UV	UV/TiO_2/H_2O_2 more efficient, biodegradability increased	[199]
16W	Biotreated	UV, UV/H_2O_2, UV/TiO_2, & UV/TiO_2/H_2O_2	UV/TiO_2 removed highest toxicity (94%) & TOC (79.6%)	[123]
30W	Mill discharged effluent	UV/H_2O_2 & UV/TiO_2/H_2O_2	UV/TiO_2/H_2O_2 capable of degrading total nitrogen and chloro-organics	[200]
UV 8W, Visible 15 W	Mill effluent	UV/TiO_2	Supported catalyst easily recovered and showed acceptable efficiency after recycling	[201]
125W solar	Mill effluent	UV/H_2O_2 & UV/TiO_2/H_2O_2	All processes removed COD (60-70%) and TOC (70-90%)	[202]
252W	Mill effluent (C & E stage of $CE_{OP}HH$)	UV, UV/NaOCl, UV/TiO_2/NaOCl, & biological treatment	30-50% COD removal after 6 h by UV/TiO_2/NaOCl, biological with UV/TiO_2/NaOCl resulted in 81 and 93% degradation after 2 h	[203]
Sunlight	Mill effluent	Solar/TiO_2/H_2O_2	Within 180 min 70.5% COD removal achieved, 80.4% total solids removed, improved BOD/COD ratio	[204]
Solar	Mill effluent	UV/TiO_2/Fe(III)	78% color, 65% TOC, and 68% AOX removed	[205]
24W	Lignin and 2,4-DCP	UV/TiO_2/H_2O_2 (fixed film)	75.1 and 94.1% lignin and 2,4-DCP removed within 420 min	[206, 207]

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CHAPTER 2
MATERIALS AND METHODS

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2.1 MATERIALS

2.1.1 Chemicals

Titanium dioxide (TiO_2) and hydrogen peroxide (30% H_2O_2) (Fisher Scientific, SQ grade) were used as photocatalyst and oxidant, respectively, for the photocatalytic oxidation experiments and the latter was also used in alkaline extraction (E_P stage) of pulp. Various isomers of chlorophenols (CP), used as reference compounds, were received from Aldrich, USA. Chlorocatechols (CC), chloroguaiacols (CG), chlorovanillin (CV), chlorosyringaldehyde (CSA), chlorosyringol (CS), chloro-resin and fatty acids (cRFA) were obtained from Helix Biotech. Corporation (Richmand, BC Canada). All the standards were of the highest purity commercially available. HPLC grade *n*-hexane, acetone, methyl tertiary butyl ether (MTBE), methanol, LR grade diethyl ether and ethanol were used as solvents. Analytical grade acetic anhydride was used after double distillation. Other reagents and chemicals used were of analytical grade and used without further purification. n-methyl-n-nitrosotoluene-p-sulphonamide was supplied by Aldrich, USA. Stock standard solutions of chlorophenolics (20-30 mg/L) and cRFA (20-30 mg/L) were prepared in acetone/water (10:90) and methanol/diethyl ether (10:90) solutions, respectively. The pH of the pulp and the aqueous solutions was adjusted with 1M H_2SO_4 or NaOH solutions. Sodium chlorite ($NaClO_2$) solution was used for in-situ generation of chlorine dioxide (D or D/C stage). NaOH solution was used for the alkaline extraction (E or E_P stage). Chlorine bleach liquor for D/C stage bleaching was procured from a paper mill in India.

2.1.2 Pulp and effluent

The unbleached mixed hardwood (Eucalyptus:Poplar, 70:30) kraft pulp was procured from a paper mill in India. The pulp was hand washed with plenty of water, screened, air dried, and stored in air tight polythene bags for further bleaching experiments in the laboratory. For generating effluent, the pulp was bleached to a target brightness of 87% ISO following D/CED, DED, DE_PD, and ODED sequences under the controlled laboratory conditions. D/C, D, E, E_P, and O refer to chlorination using 50% substitution by chlorine dioxide, chlorine dioxide, alkaline extraction, peroxide reinforced alkaline extraction, and oxygen delignification stages, respectively. Effluent of individual bleaching stages was collected. The primary clarified (PC) and biotreated (BT) paper mill effluents were collected from the effluent treatment plants of two pulp and paper mills located in India. Mill A uses OCE_PHH while Mill B uses $D/CE_{OP}DD$ sequence for bleaching the mixed hardwood (Eucalyptus and Poplar) kraft pulp. The laboratory generated and paper mill effluents were stored in a refrigerator below 4 °C for subsequent photocatalytic studies.

2.2 PULP BLEACHING

The experimental conditions followed during different stages of D/CED, DED, DE_PD, and ODED sequences to bleach the pulp to a target brightness of 87% ISO are listed in Tables 2.1 and 2.2. Chlorine demand on the pulp was calculated using the following formula:

$$Chlorine\ demand\ (\%\ aCl^-) = Kappa\ no. \times Kappa\ factor \qquad (2.1)$$

Of the total chemical dose, 70% was given in the first (D_1 or D/C) stage and remaining 30% in last stage (D_2). All the bleaching experiments were performed in polythene bags except D/C stage which was performed in plastic bottles at ambient temperature. All the bleaching experiments were performed with 200 g O.D. unbleached pulp. The disintegrated pulp was adjusted to desired consistency and pH. Bleaching chemicals were added to the pulp, hand mixed, and placed in the water bath at desired temperature. The pulp was well kneaded by hand mixing or shaking the bottle from time to time during bleaching. After bleaching, the pulp slurry was filtered and filtrate was collected. The pulp was washed with distilled water in a Buchner funnel. The filtrate and washings were mixed and stored in refrigerator below 4 °C for characterization and photocatalytic oxidation studies. All the bleaching experiments were performed in duplicate and average values reported.

2.2.1 Pulp disintegration

Before bleaching and oxygen delignification the air dried pulp was soaked in water overnight and disintegrated (to break the fibre bundles and lumps) at 3% consistency for 4-5 min using a laboratory pulp disintegrator. The water was drained away on a screen and the disintegrated pulp was squeezed and placed in refrigerator below 4 °C in plastic bags. The wet disintegrated pulp was used for further bleaching experiments within one week.

2.2.2 Pulp sheet preparation

The consistency of the disintegrated pulp suspension was set to 1% and transferred to a Buchner funnel. The water was then drained away through a screen of 22 mesh size, so as to give a sheet of about 5 g O.D. weight. The wet pulp sheet was picked with the help of two blotting papers and then pressed using a hydraulic press to remove excess water. The sheet was air dried and protected against dirt and dust. The brightness was measured within 24 h after drying. For kappa number and viscosity measurement the sheet was cut into small test pieces.

2.2.3 Oxygen delignification (O) stage

Oxygen delignification stage was performed in laboratory autoclaves (100 g O.D. pulp) revolving in hot ethylene glycol bath. NaOH (1-3% on O.D. basis) and $MgSO_4$ (0.2% on O.D. basis) were added to the disintegrated pulp and desired consistency (10%) was set. The pulp was hand mixed and transferred into autoclaves which were then filled with oxygen to a pressure of 6 kg/cm^2 after expelling air. The autoclaves were then placed in ethylene glycol bath at 100 °C for 75 min [1]. After completion of the reaction autoclaves were taken out and cooled to room temperature. Pulp was taken out and washed with plenty of water on a screen. The excess water was drained off by squeezing and the pulp was stored in polythene bags for further bleaching experiments. Alkali charge was varied between 10-30 kg/t O.D. pulp for achieving a kappa number drop between 40-50% without sacrificing much on pulp viscosity. The oxygen delignified pulp was characterized for kappa number, viscosity, and brightness.

2.2.4 Chlorine dioxide/chlorine (D_{50}/C_{50}) stage

The disintegrated pulp was diluted with distilled water and pH was adjusted using 1M H_2SO_4 or NaOH solutions, so that end pH remains near 2 and pulp consistency 3% even after adding the bleach liquors. First calculated quantity of $NaClO_2$ bleach liquor equivalent to 50% substitution and then chlorine bleach (Cl_2) liquor were added to the pulp. The bleaching was performed in air tight plastic bottles. Cl_2 bleach liquor was added to the pulp with the help of a funnel having a rubber tube attached to it which reaches to the bottom of the bottle. Thus any leakage of chlorine gas was prevented. The bottle was tightly capped and contents were shaken well intermittently. The reaction was performed at ambient temperature for 45 min. After bleaching, pulp was filtered and washed with distilled water. Filtrate and washings were mixed and stored for the measurement of residual active chlorine, end pH, characterization in terms of BOD, COD, color, AOX, chlorophenolics, and cRFA, and photocatalytic oxidation studies.

2.2.5 Chlorine dioxide (D) stage

The disintegrated pulp was diluted with distilled water and pH was adjusted between 3 and 4 with 1M H_2SO_4 or NaOH solutions. The required quantity of $NaClO_2$ bleach liquor was added to the pulp and mixed. The bleaching was performed at 10% consistency in polythene bags suspended into the water bath at 70 °C temperature for 3 h. The pulp suspension was mixed intermittently. After bleaching, the plastic bags were removed and pulp was filtered and washed with distilled water. Filtrate and washings were mixed and stored for measurement of residual active chlorine, end pH, characterization in terms of BOD, COD, color, AOX, chlorophenolics, and cRFA, and photocatalytic oxidation studies.

2.2.6 Alkaline extraction (E) stage

The calculated amount of NaOH solution and distilled water were mixed with the disintegrated pulp to give a pulp consistency of 10% in polythene bag. The polythene bag was suspended into the water bath maintained at 70 °C temperature for 90 min. The pulp was kneaded intermittently for proper mixing. After alkaline extraction, pulp was washed and effluent collected for measurement of end pH, characterization in terms of BOD, COD, color, AOX, chlorophenolics, and cRFA, and photocatalytic oxidation studies.

2.2.7 Peroxide reinforced alkaline extraction (E_P) stage

For peroxide reinforced alkaline extraction stage 0.3% H_2O_2 on O.D. pulp basis was added to the pulp suspension along with alkali, all other parameters were same as of E stage. After completion of the reaction, the pulp was washed and effluent collected for measurement of end pH, characterization in terms of BOD, COD, color, AOX, chlorophenolics, and cRFA, and photocatalytic oxidation studies.

2.3 EFFLUENT TREATMENT

2.3.1 Photocatalytic reactor

The photocatalytic oxidation experiments were carried out in a borosilicate glass bowl (1L). The glass bowl containing the reaction mixture was placed in a timber-framed UV reactor (77 cm × 36 cm × 71 cm) equipped with 4 UV (Ultra Violet) tubes ($\lambda = 365$ nm) each of 18 W (Philips) on the top side, located at a distance of 15 cm from the sample (Figure 2.1). The reaction mixture was subjected to irradiation under UV light with continuous stirring. A fan fitted on the side wall was used to lower the heat generated by UV tubes. All the experiments were carried out in completely mixed and batch mode.

2.3.2 Optimization of treatment parameters

The effect of the various reaction variables, i.e. catalyst dose (0.25 to 1.5 g/L), pH (3.0 to 8.0), reaction time (0.5 to 8 h), UV intensity, organic load (325 to 995 mg/L COD), and H_2O_2 concentration (5 to 75 mM/L), on the photocatalytic oxidation of pollutants present in paper mill effluent was examined. The degradation of pollutants was quantified in terms of the percentage removal of COD and color of the effluent after photocatalytic oxidation (2.2).

$$Degradation\ (\%) = [(C_0 - C)/C_0] \times 100 \tag{2.2}$$

Where: C_0 = initial concentration; C = concentration after photodegradation.

2.3.3 Photocatalytic oxidation

A 500 mL (diluted) aliquot of bleaching/ paper mill effluent was adjusted to the desired pH and transferred to the glass bowl. An appropriate amount of TiO_2 was added and the aqueous suspension was magnetically stirred for 30 min before adding H_2O_2 and switching on UV tubes. The experiments were carried out at ambient temperature. The solar experiments were carried out on sunny days of summer (May and June) under clear skies between 10 A.M. to 2 P.M. After completion of the reaction, water loss was made up by distilled water, the solution was adjusted to pH 7.0 and allowed to settle for 5 h. Supernatant was collected and TiO_2 agglomerates were removed by centrifugation before analysis. The effluent was characterized before and after photocatalysis in terms of BOD, COD, color, AOX, chlorophenolics, and cRFA as mentioned in analytical methods section (2.4.8). The change in biodegradability index (BOD/COD) of the effluents was also investigated for assessing the biodegradability of organic pollutants. The effluent after treatment was analyzed for residual H_2O_2 by the iodometric method [2]. All the analyses were performed in duplicate and the average values have been reported.

2.3.4 Catalyst separation and recycling

The catalyst separation was carried out by increasing the pH of the effluent after treatment by dilute NaOH solution to attain the zero charge and allowing the catalyst to be settled [3, 4]. After photocatalytic treatment, the effluent suspension was adjusted to pH 7.0 and left for 5 h for the catalyst sedimentation. The catalyst sediment was collected and the supernatant was discarded. The sediment was dried in oven at 100 °C temperature and weighed to find out loss of catalyst along with the supernatant. The recovered catalyst (undried) was reused in the next photocatalysis experiment and the lost amount of the catalyst was made up by adding fresh catalyst. The whole cycle of effluent treatment, catalyst sedimentation, recovery, and reuse was repeated five times and efficiency for COD and color removal was observed.

2.4 ANALYTICAL METHODS

2.4.1 Pulp characterization

The brightness was measured with the help of TECHNIBRITE ERIC 950 from Technibrite Corporation, USA [5]. The various test methods used for preparation and characterization of the pulp and paper hand sheets are listed in Table 2.3. The photographic view of pulp Tear tester, Tensile tester, and Burst tester is shown in Figure 2.2 (a-c).

2.4.2 Pulp viscosity measurement

The viscosity of the pulp suspension was measured by capillary viscometer method using 1 M cupriethylenediamine (CED) solution. TAPPI test method (T 230 om-99) was followed. The viscometer constant was determined using glycerol solution of known specific gravity and viscosity. The constant thus obtained was used for further viscosity calculations. The pulp sample equivalent to 0.25 g O.D. was taken into a 50 mL dissolving bottle containing 2-3 copper beads. Exactly 25 mL of distilled water was added to the bottle, capped, gently shaken for dispersing the pulp, and left for 2 min. Exactly 25 mL of CED solution was added to the pulp suspension and purged with nitrogen for 1 min. The bottle was capped and shaken until the fiber is completely dissolved (about 15 min). After shaking, bottle was kept for 2 min to allow the solution to degas. The viscometer was placed in a constant temperature bath at 25±0.1 °C for attaining constant temperature. The measuring leg of the viscometer was immersed into the solution and filled by suction up to the upper mark. Then the solution was allowed to drain down. The efflux time was determined by measuring the time required for the meniscus to pass between the two marks. The efflux time measurement was repeated and the pulp viscosity was calculated by using the following formula:

$$V = C \times t \times d \qquad (2.3)$$

Where:

V = viscosity of CED solution at 25 °C (cP)
C = viscometer constant found by calibration
t = average efflux time (seconds)
d = density of the pulp solution ($g/cm^3 = 1.052$)

2.4.3 Bleach liquor analysis

A solution of 40 g/L of $NaClO_2$ was prepared in distilled water. Strength of $NaClO_2$ solution or chlorine water, as active chlorine (aCl^-), was determined by titrating against standard 0.1 N $Na_2S_2O_3$ solution using starch (0.5%) as indicator. To 10 mL of diluted bleach liquor ($NaClO_2$ solution or chlorine water) 10 mL KI (10%) and 10 mL acetic acid (10%) were added and the resulting solution was titrated against standard $Na_2S_2O_3$ solution. End point was blue to colorless. Strength of the bleach liquor was calculated using the following formula:

$$Strength\ of\ bleach\ liquor\ (g/L) = Normality\ of\ bleach\ liquor \times 34.5 \qquad (2.4)$$

2.4.4 Residual chlorine analysis

Same procedure as mentioned above was followed for the determination of residual chlorine in the spent bleach liquor. Here, 100 mL of spent bleach liquor was titrated against standard 0.01 N $Na_2S_2O_3$ solution [1].

2.4.5 Hydrogen peroxide analysis

10 mL of H_2O_2 solution was diluted to 250 mL in a volumetric flask. 10 mL KI (10%), 10 mL H_2SO_4 (4N), and 1 mL ammonium molybdate (1%) were added to 5 mL of this solution

and the resulting solution was titrated against standard 0.1 N $Na_2S_2O_3$ solution using starch (0.5%) as indicator [6]. The end point was blue to colorless. Strength of H_2O_2 solution was calculated using the following formula:

$$Strength\ of\ H_2O_2\ (g/L) = Normality\ of\ H_2O_2 solution \times 34 \qquad (2.5)$$

2.4.6 Characterization of catalyst

The phase composition of TiO_2 was analyzed by X-ray Diffractometer (Bruker AXS D8) using Cu Kα radiation (λ = 1.5406 A°), in the following conditions: range (2θ) = 10-60°, accelerating voltage = 40 kV, emission current = 30 mA, and step size (2θ) = 0.019° (9.6 s per step). The weight fraction of anatase (W_A) and rutile (W_R) was determined using the following formula:

$$W_R = 1.26I_R/(I_A + 1.26I_R) \qquad (2.6)$$

Where, I_A and I_R are relative intensities of the strongest diffraction peaks of anatase and rutile, respectively [7]. TiO_2 crystallite size and morphology were observed by field emission scanning electron microscopy (FE-SEM) (FEI Quanta 200 F) at 20 kV. TiO_2 powder was dispersed in acetone by placing it in an ultrasonic bath for 15 min. One drop of the dispersion was poured over a glass plate affixed on the aluminium stub, and it was allowed to dry. The sample was subjected to gold coating before FE-SEM analysis to ensure conductivity. The elemental composition was investigated using energy dispersive X-ray analysis (EDX) (FEI Quanta 200 F). The adsorbed water and hydroxyl groups on the surface of TiO_2 were analyzed by fourier transform infrared spectroscopy (FTIR) (NICOLET 6700 spectrophotometer, Thermo Scientific) using KBr pellets (wave number range 400-4000 cm^{-1}). Brunauer-Emmett-Teller (S_{BET}) surface area and total pore volume measurements were carried out by N_2 adsorption (Micromeritics, Chemi Soft TPx V1.02).

2.4.7 Light intensity measurement

The light intensity was measured using ferrioxalate actinometer. The green crystals of $K_3[Fe(C_2O_4)_3].3H_2O$ were prepared by mixing 3 vol of 1.5 M $K_2C_2O_4$ with 1 vol of 1M $FeCl_3$ solution, recrystallized three times from warm water, dried at 45 °C and kept in the dark. 0.006 M solution was prepared by dissolving 2.947 g of the crystals in 100 mL of H_2SO_4 (0.5 M) and diluted with distilled water to 1 L. An absorption spectrum of the solution was taken. 3 mL (V_1)

of the solution was irradiated under efficient stirring. 1 mL (V_2) of the irradiated solution was taken into a 10 mL (V_3) volumetric flask containing a mixture of 4 mL of 1,10-phenanthroline solution (0.1%) and 0.5 mL of buffer (82 g $NaC_2H_5CO_2$ and 10 mL conc. H_2SO_4, diluted to 1 L with distilled water) which was then diluted to the mark with distilled water. A reference solution without irradiation was prepared in the same way. Both solutions were kept in the dark (about 1h) until full color development is achieved, and the absorbance difference between the two samples was measured at 510 nm [optical path length l = 1cm, ε (510 nm) = 11100 L^3 $mol^{-1}cm^{-1}$]. A (510 nm) should be within the range 0.4-1.8. The photon flux, amount basis, $q_{n,p}$/Einstein s^{-1}, entering the sample cell is given by the following formula:

$$q_{n,p} = \frac{\Delta A V_1 V_3}{\emptyset(\lambda)\mathcal{E}(510\ nm)V_2 l t} \tag{2.7}$$

with t = irradiation time. At room temperature $\emptyset(\lambda)$ = 1.20-1.26 (0.006 M) for the wavelength range 254-366 nm [8]. The photon flux was measured to be 2.28 × 10^{-6} q_{np}/Einstein s^{-1} at a distance of 15 cm from UV lamps. At this we obtained optimum photocatalytic treatment efficiency. The solar radiation during May and June months remained between 30-50 W/m^2 [9].

2.4.8 Effluent analysis

The pulp bleaching (individual stage) and paper mill effluents (PC and BT) were characterized for color (Pt-Co method, measured at 465 nm using UV-VIS spectrophotometer, SPEKOL 2000, Analytic Jena), pH, BOD (by measuring dissolved oxygen before and after incubation at 20 °C for 5 days), COD (determined by closed reflux titrimetric method) [10], AOX (analyzed on AOX analyzer, ECS 1200, using column method), chlorophenolics [Thermo Electron Corporation Gas chromatograph (Trace GC Ultra) - Mass spectrometer (MS, DSQ)] [11, 12], cRFA (Thermo Electron Corporation Gas chromatograph) [13, 14] before and after photocatalytic oxidation. The photographic view of GC-MS and AOX analyzer is shown in Figure 2.3 (a and b).

2.5 COLOR MEASUREMENT

2.5.1 Preparation of standard color solution

250 mg metallic Pt (99.99% pure) was dissolved in aqua regia with the aid of heat. This solution was heated to dryness to remove excess of HNO_3 (as oxides of nitrogen) by repeated

evaporation and addition of fresh portions of concentrated HCl. The residue was dissolved in distilled water along with 500 mg of crystallized $CoCl_2.6H_2O$ (equivalent to 125 mg Co) and 5 mL of concentrated HCl. The total volume of the solution was made up to 100 mL with distilled water to yield a standard solution of 2500 Pt-Co color units (mg/L) [10].

2.5.2 Color measurement

Standard solutions of 50, 100, 250, 500, 750, 1000, 1500, and 2000 Pt-Co units were prepared by diluting 0.5, 1.0, 2.5, 5.0, 7.5, 10, 15, and 20 mL of standard stock solution to 25 mL in a volumetric flask. Absorbance of different standard solutions (Table 2.4) was determined at 465 nm on UV/Visible double beam spectrophotometer and calibration curve was plotted as shown in Figure 2.4. This curve was used to determine the color of the effluent. The pH of the effluent was adjusted to 7.6 and centrifuged for 5 min at 1500 rpm to remove suspended particles. Then the absorbance of the solution was measured at 465 nm and color concentration was calculated from the calibration curve.

2.6 CHLOROPHENOLICS ANALYSIS

GC-MS was used for the qualitative and quantitative analysis of chlorophenolics in the effluent. The extraction of various chlorophenolic compounds from effluent was performed by simple modification of the procedure suggested by Lindstrom and Nordin [12] using diethyl ether/ acetone (90:10) solution. The chlorophenolics were converted to readily volatilized acetyl derivatives prior to GC-MS analysis. The acylation was done with acetic anhydride based on procedure suggested by Abrahamsson and Xie [11].

2.6.1 Extraction

The chlorophenolics extraction was done with 1 L of the pulp bleaching/ paper mill/ photocatalytically treated effluent. The effluent was adjusted to pH 2 with dilute H_2SO_4 and extracted with 400 mL of diethyl ether/acetone mixture (90:10) for 48 h with intermittent shaking. Figure 2.5 depicts the schematic flow diagram of the method followed for extraction of chlorophenolic compounds from the effluent and analysis. The emulsion formed in the ether layer was broken by using a heat gun. Then the whole ethereal extract of the effluent was transferred into another separating funnel and shaken with 5 mL of $NaHCO_3$ (0.5 M) solution to remove acidic impurities. Thereafter, the ether layer was shaken with 5 mL of NaOH (0.5 M) solution for the chlorophenolics extraction. The aqueous NaOH layer, containing chlorophenolics, was separated and washed with 10 mL of fresh diethyl ether to remove the neutrals. The aqueous NaOH layer was derivatized.

2.6.2 Derivatization

In each case 4.5 mL of effluent extract (4 mL diluted to 4.5 mL with distilled water) or chlorophenolics standard (1 mL diluted to 4.5 mL with distilled water) solution was taken in a PTFE lined screw capped glass tube. 0.5 mL of Na_2HPO_4 (0.5 M) 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 tube was shaken for 5 min. The acetyl derivatives of chlorophenolics were extracted with 1 mL of n-hexane. The mixture was shaken for 3 min and 1 µL of acetyl derivative, taken from the hexane layer by a syringe, was injected into GC column by auto sampler (AI 3000) for the identification and quantitative analysis of chlorophenolics [15].

2.6.3 GC-MS conditions

TR-5 capillary column (30 m x 0.25 mm I.D. with 0.25 µm film thickness) containing 5% phenyl methyl polysiloxane was utilized for the chromatographic separation of target compounds. The oven temperature was held at 45 °C (1 min) and increased to 280 °C at 6 °C/min, keeping the final temperature for 25 min. Injector, mass transfer line, and ion source temperatures were set at 210 °C, 280 °C, and 200 °C, respectively. The carrier gas was helium (He) at a flow rate of 1 mL/min. MS was operated in the electron impact ionization (EI) mode with an ionizing energy of 70 eV and an emission current of 100 µA. Full scan data were obtained by scanning from 42-336 m/z at a scan speed of 216.7 amu/sec (0.7241 scans per second) and fore pressure 38-45 mTorr. Target compounds in the effluent were first identified by matching their mass spectrum with that obtained from NIST library. Once main peaks were identified, pure standard solutions of target compounds were injected into GC-MS system for determining retention times (RT). All injections were made in the splitless (1 min) mode.

2.7 CHLORO-RESIN AND FATTY ACIDS ANALYSIS

Gas chromatograph (GC) was used for the qualitative and quantitative analysis of cRFA present in the effluent. The extraction of target compounds from effluent has been achieved as suggested by Voss and Rapsomatiotis [13]. cRFA were converted to their readily volatilized methyl esters prior to GC analysis. Methylation was done with diazomethane according to the procedure suggested by Vogel [14].

2.7.1 Diazomethane preparation

Smaller quantities of diazomethane were prepared from Diazald. 2.14 g of N-methyl-N-nitrosotoluene-p-sulphonamide was dissolved in 30 mL of diethyl ether and the solution was cooled in ice. Then after an ethereal KOH solution (0.4 g KOH dissolved in 10 mL of ethanol/ water, 96:4) was added. The addition of ethanol was continued till the solution was clear and no precipitate was present. After 5 min the ethereal diazomethane solution was distilled. The ethereal solution contained 0.32-0.35 g of diazomethane [14].

2.7.2 Extraction

Extraction of cRFA was done from 100 mL of the pulp bleaching/ paper mill/ photocatalytically treated effluent. The effluent was adjusted to pH 9.0 and extracted with equal volume of MTBE for 1 h. The ether layer, containing extracted cRFA, was separated and concentrated in a rotary vacuum evaporator. The concentrate was evaporated to almost dryness (approximately 0.5 mL) with a flow of N_2 (Figure 2.6). It was then dissolved in 0.1 mL of methanol/diethyl ether (10:90) solution and derivatized.

2.7.3 Derivatization

cRFA were derivatized by using ethereal solution of diazomethane. In each case, 0.1 mL effluent extract/ cRFA standard solution was derivatized with dropwise addition of ethereal solution of diazomethane till a pale yellow color persisted for some time. The excess diazomethane was destroyed by dropwise addition of glacial acetic acid. The resulting solution was diluted with methanol/ diethyl ether (10:90) solution and the total volume was made up to 1 mL. 0.5 μL of this solution was injected into GC column for the analysis of cRFA.

2.7.4 GC conditions

Analysis of cRFA as methyl esters was performed on GC. Chromatographic separation was done on OPTIMA -1- MS column (30 m x 0.25 mm I.D. with 0.25 μm film thickness) containing 100% dimethyl polysiloxane. Detection and identification was carried out with a flame ionization detector (FID) at 10^0 range. The oven temperature was held at 190 °C (4 min) and increased to 210 °C at 1 °C/min, from 210 °C to 230 °C at 2 °C/min, from 230 °C to 250 °C at 3 °C/min, keeping the final temperature 250 °C for 15 min. Injector and detector temperatures were set at 300 °C. The carrier gas was nitrogen (N_2) at a flow rate of 1 mL/min. The target analytes were identified by comparing the retention times (RT) (±0.1 min) with those of derivatized standards. All injections were made in the splitless mode (1 min).

2.8 QUANTITATIVE ANALYSIS

The quantitative analysis of chlorophenolics and cRFA was performed with the help of calibration curve and extraction efficiency determination. The calibration curves of individual chlorophenolic compounds were prepared by measuring the peak areas by injecting different concentrations of pure standard solutions.

2.8.1 Extraction efficiency (EE) determination

For extraction efficiency determination, 1 mL of standard solution of each chlorophenolic compound was diluted to 1 L with distilled water. The pH of the solution was adjusted to 2.0. Similarly, 1 mL of standard solution of each cRFA was diluted to 100 mL with distilled water and pH was adjusted to 9.0. Both these solutions were then extracted and derivatized as described earlier for chlorophenolics (Section 2.6.1 and 2.6.2) and cRFA (Section 2.7.2 and 2.7.3). The derivatives of chlorophenolic (1 µL) and cRFA (0.5 µL) compound were injected into GC-MS and GC columns, respectively, and the peak areas were determined. The quantity present in the extracted sample was determined from the peak area. EE (%) was calculated according to the following formula:

$$Extraction\ efficiency\ (\%) = \frac{Quantity\ in\ the\ extracted\ sample}{Quantity\ in\ the\ sample\ before\ extraction} \times 100 \qquad (2.8)$$

2.8.2 Response factor (RF) determination

For response factor determination, 1 mL of standard solution of cRFA was derivatized and the methyl esters (0.5 µL) were injected into GC column. The area of the peak was recorded and RF was calculated according to the following formula:

$$RF = \frac{Area\ of\ the\ peak}{Wt.\ of\ the\ sample\ injected\ (pg)} \qquad (2.9)$$

Table 2.1 Pulp bleaching conditions for different stages of D/CED and DED sequences

Parameter	D/CED			DED		
	D_{50}/C_{50}	E	D	D_1	E	D_2
Kappa no.	15			15		
Kappa factor	0.30			0.35		
Total aCl^- (% O.D. pulp)	4.50			5.25		
Bleach chemical (% aCl^-)	3.15 (50:50)	----	1.35	3.68	----	1.57
Residual aCl^- (%)	Nil	----	0.23	Nil	----	0.03
NaOH (% O.D. pulp)	----	1.0	----	----	0.7	----
Consistency (%)	3	10	10	10	10	10
End pH	2.0	10.5	3.5	3.4	11.5	3.5
Temperature (°C)	Ambient	70	70	70	70	70
Time (min)	45	90	180	180	90	180
Brightness (% ISO)	86.9			87.1		

Table 2.2 Pulp bleaching conditions for different stages of DE_PD and ODED sequences

Parameter	DE_PD			ODED			
	D_1	E_P	D_2	O	D_1	E	D_2
Kappa no.	15			15 (8.3 after O stage)			
Kappa factor	0.30			0.30			
Total aCl^- (% O.D. pulp)	4.5			2.49			
Bleach chemical (% aCl^-)	3.15	----	1.35	----	1.74	----	0.75
Residual aCl^- (%)	Nil	----	0.04	----	Nil	----	Nil
NaOH (% O.D. pulp)	----	0.7	----	2.0	----	0.7	----
H_2O_2 (% O.D. pulp)	----	0.3	----	----	----	----	----
Consistency (%)	10	10	10	10	10	10	10
End pH	3.5	10.5	3.3	----	3.5	11.4	3.2
Temperature (°C)	70	70	70	100	70	70	70
Time (min)	180	90	180	75	180	90	180
O_2 pressure (kg/cm^2)	----	----	----	6	----	----	----
$MgSO_4$ (%)	----	----	----	0.2	----	----	----
Brightness (% ISO)	87.3			86.9			

Table 2.3 Test methods for preparation and characterization of pulp and paper sheets

Test No.	Description
SCAN C 18 : 65	Disintegration of chemical pulp for testing
T 248 sp - oo	Laboratory beating of pulp (PFI mill method)
T 205 sp - 95	Forming hand sheets for physical tests of pulp
T 218 sp - 97	Forming hand sheets for reflectance testing of pulp (buchner funnel procedure)
T 227 om - 99	Freeness of pulp (canadian standard method)
T 410 om - 98	Grammage of paper and paperboard (weight per unit area)
T 230 om - 99	Viscosity of pulp (capillary viscometer method)
T 236 om - 99	Kappa number of pulp
T 403 om - 97	Bursting strength of paper
T 404 cm - 92	Tensile breaking length and elongation of paper and paperboard (using pendulum type tester)
T 414 om - 98	Internal tearing resistance of paper (elmendorf-type method)
ISO Standard 2469	Brightness of pulp
T 610 sp - 97	Preparation of indicators and standard solutions

Table 2.4 Absorbance of standard color solutions

S. No.	Concentration (mg Pt-Co units/L)	Absorbance
1.	50	0.012
2.	100	0.027
3.	250	0.066
4.	500	0.125
5.	750	0.198
6.	1000	0.264
7.	1500	0.382
8.	2000	0.510
9.	2500	0.660

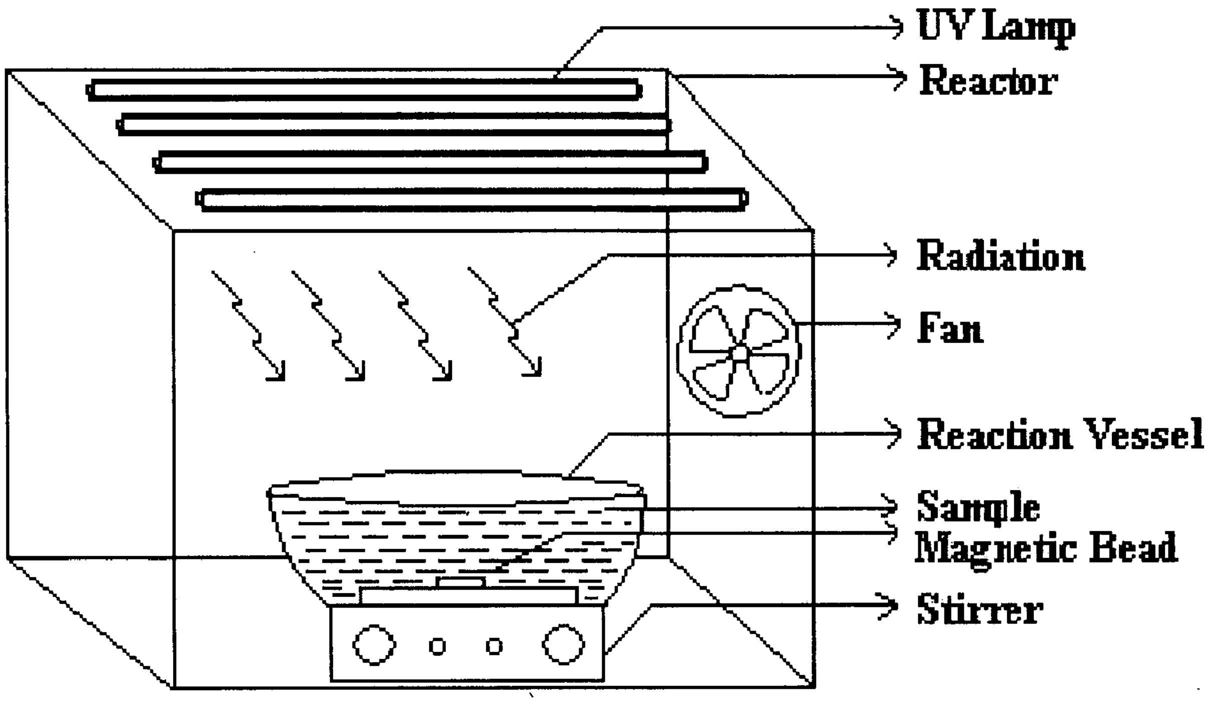
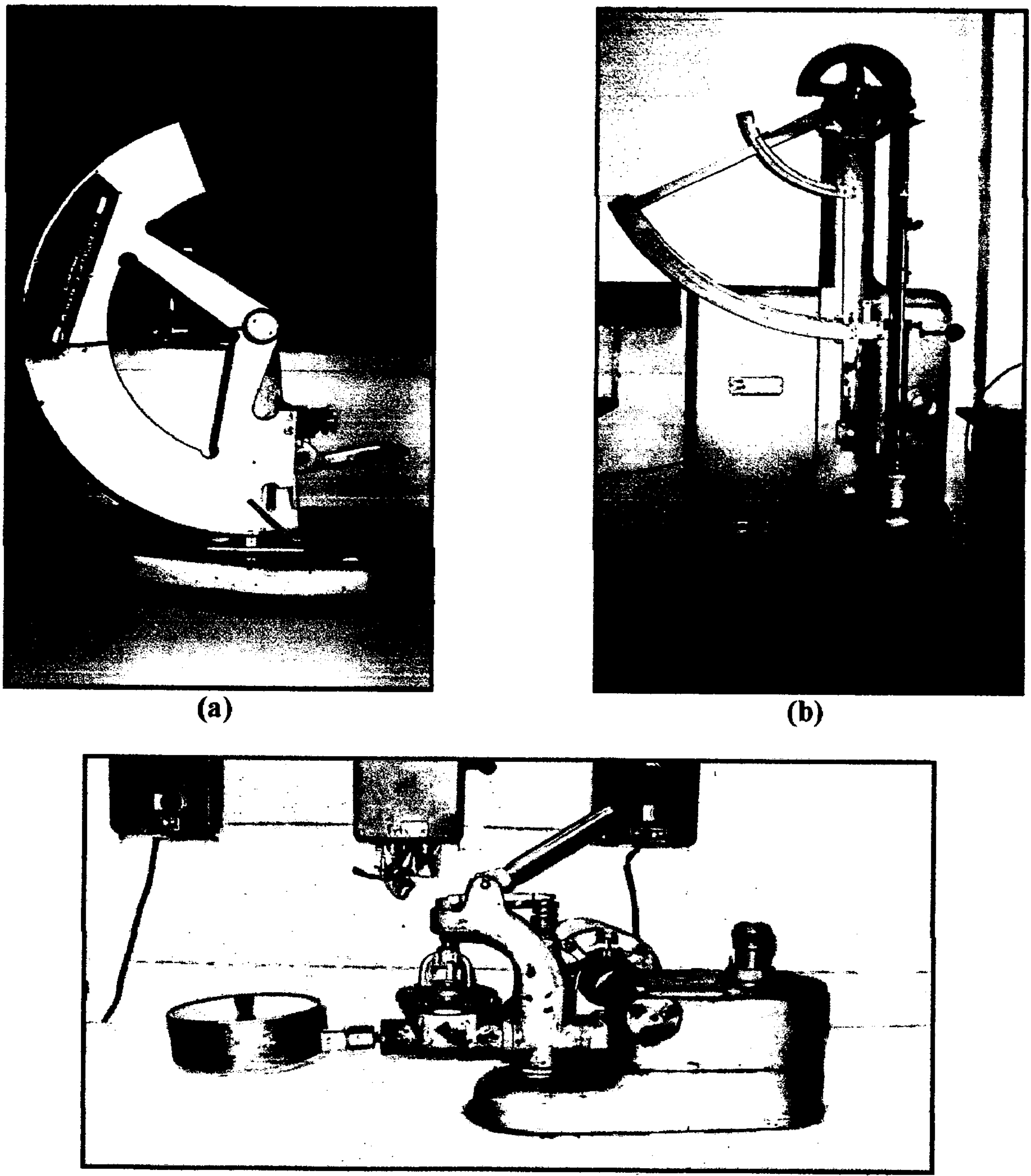


Figure 2.1 Experimental set-up for the photocatalytic oxidation of effluent

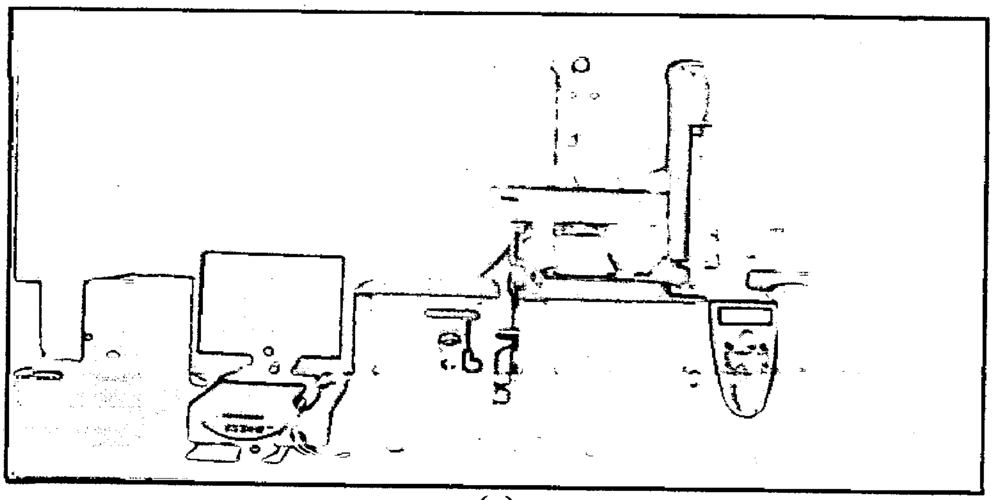


(a)

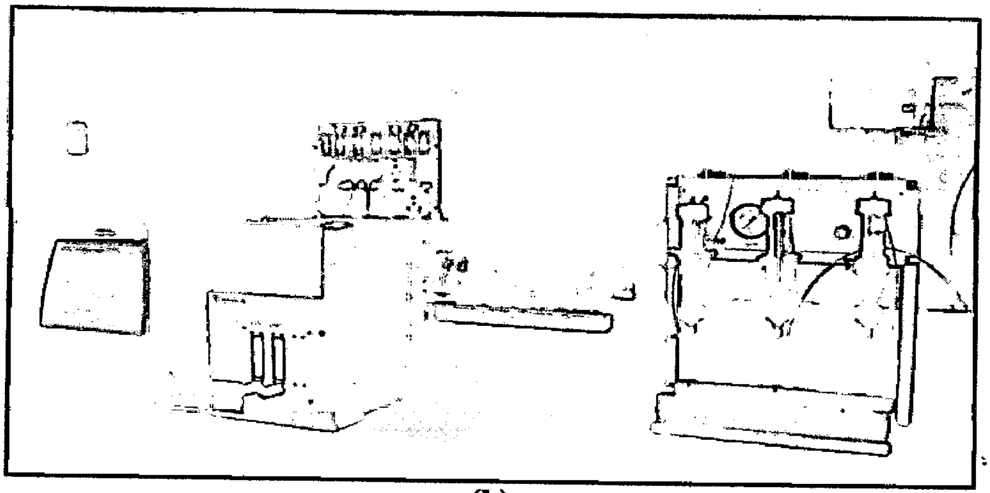
(b)

(c)

Figure2.2 Photographic view of (a) Tear tester, (b) Tensile tester, and (c) Burst tester



(a)



(b)

Figure 2.3 Photographic view of (a) GC–MS and (b) AOX analyzer

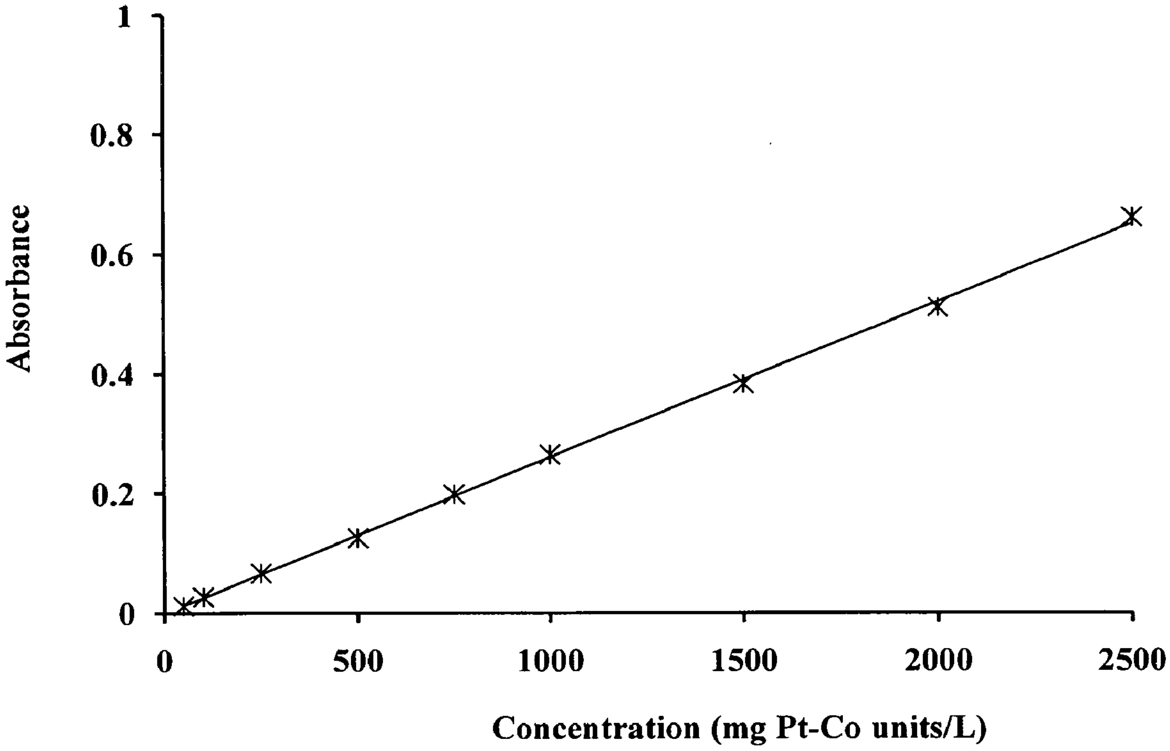


Figure 2.4 Calibration curve used for effluent color estimation

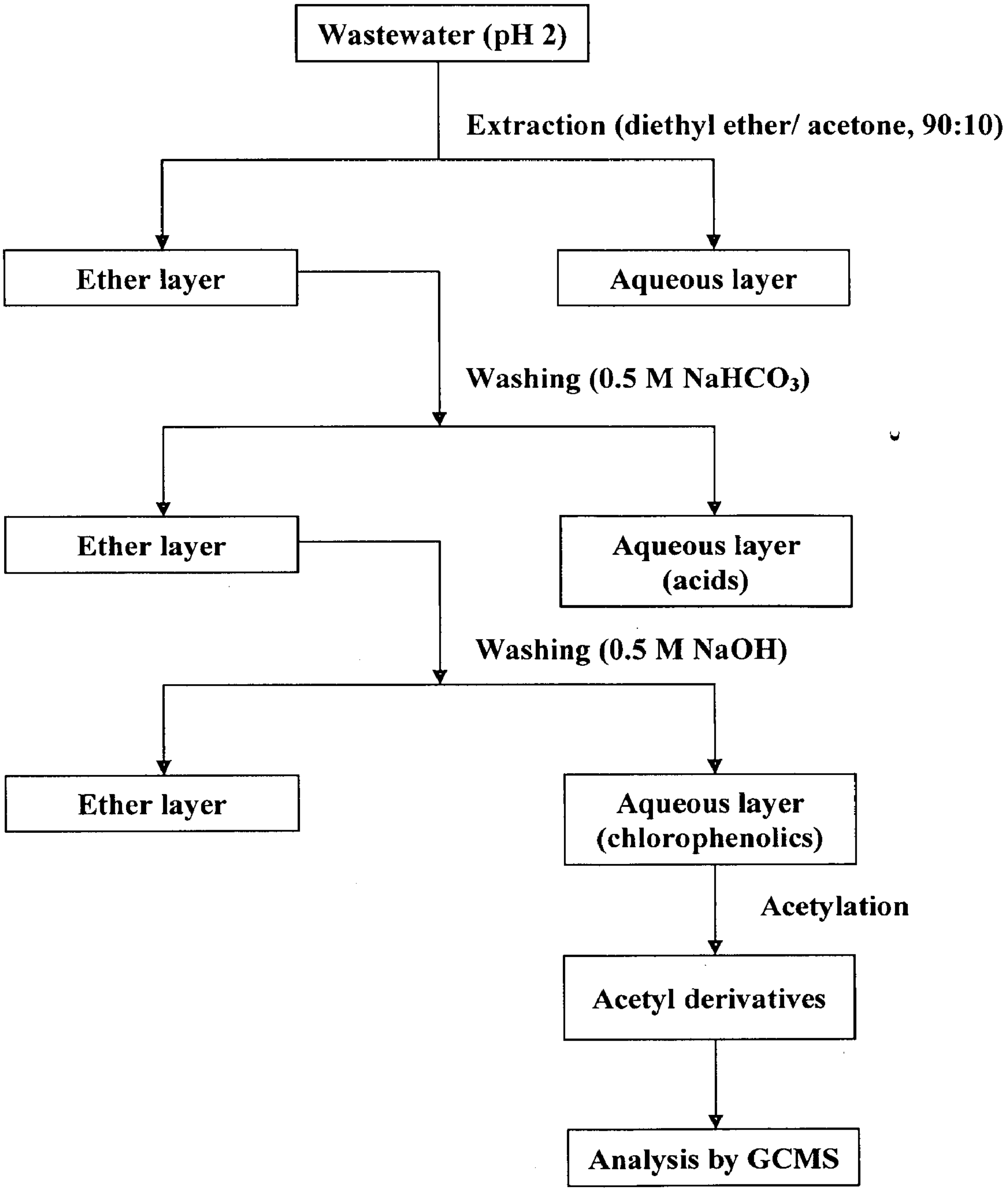


Figure 2.5 Extraction of chlorophenolic compounds from effluent and analysis

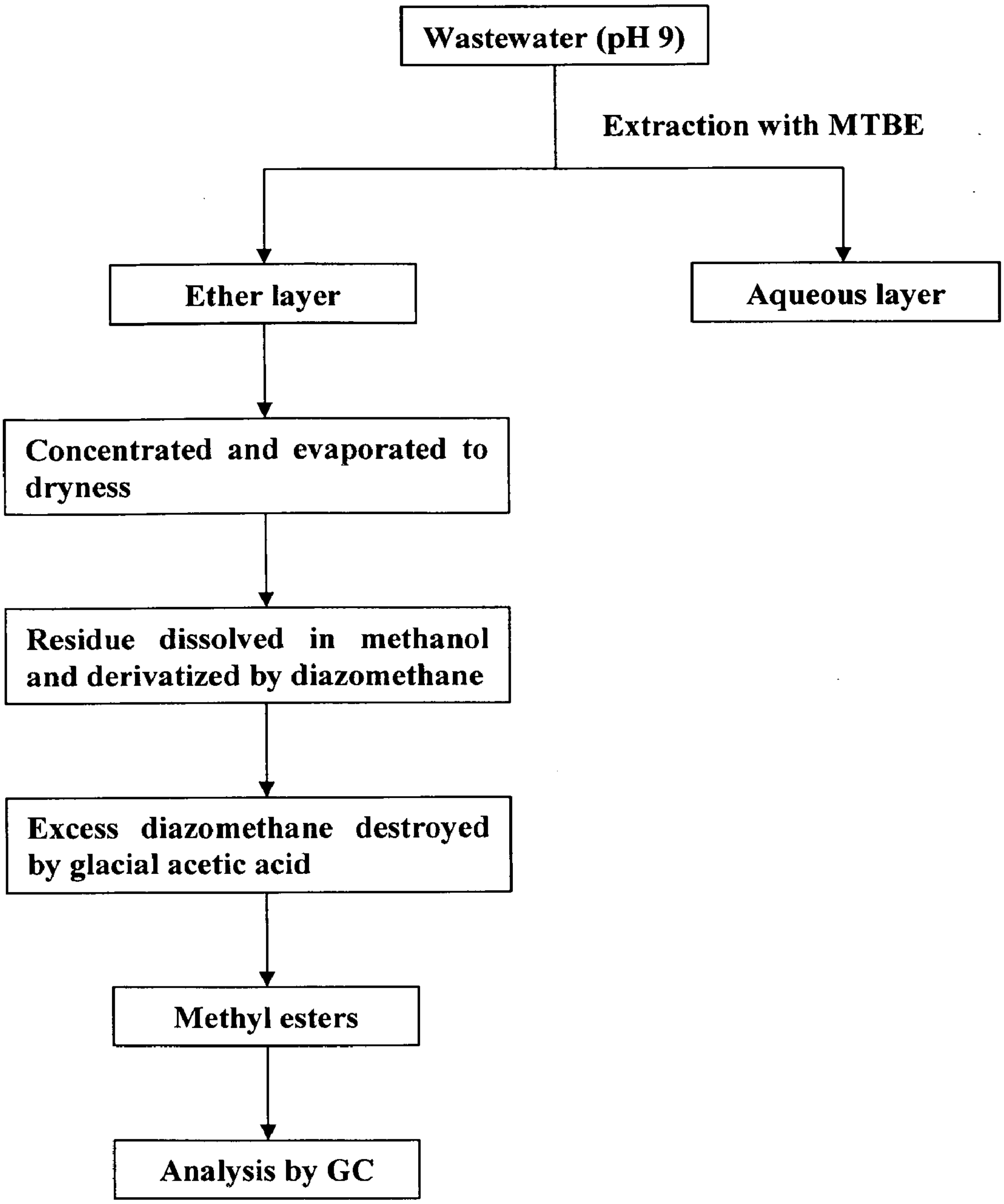


Figure 2.6 Extraction of chloro-resin and fatty acid compounds from effluent and analysis

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CHAPTER 3
PULP BLEACHING STUDIES

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PULP BLEACHING STUDIES

3.1 INTRODUCTION

Bleaching is a chemical process applied to cellulosic materials to achieve the desirable pulp brightness. The residual lignin is responsible for the undesirable dark color and for the photo-yellowing of the pulp. Bleaching process increases the pulp brightness by either lignin removal or decolorization [1]. When chlorine (Cl_2) or chlorine based chemicals are used for pulp bleaching a variety of chlorinated organics, i.e. phenols, chloro-resin and fatty acids (cRFA), and polychlorinated dioxins and furans etc. collectively estimated as adsorbable organic halides (AOX), are found in the bleach plant effluents [1-3].

The growing environmental concern regarding the impact of bleach plant effluents has led to the progressive substitution of hazardous Cl_2 based conventional pulp bleaching with environment friendly technologies for the regulation of chlorinated organic matter, AOX, in the effluents [1, 4]. The bleach plant pollution abatement can be done by using two approaches:

(1) In-plant technology modification for reducing generation of AOX.

(2) End-of-pipe treatment of effluent for further reducing pollution load.

AOX generation can be decreased by reducing the amount of Cl_2 used for the bleaching. Cl_2 requirement can be decreased by pre-chlorination modifications, chlorination stage changes, and post chlorination modifications [5]. Pre-chlorination modifications, i.e. extended delignification [6] and oxygen (O_2) delignification [7], reduce the chemical charge required for bleaching by decreasing the incoming pulp kappa number and thus reduce AOX generation correspondingly. The replacement of molecular chlorine by chlorine dioxide (ClO_2) in the elemental chlorine free (ECF) bleaching process also decreases the amount of chlorinated organics formed [1]. After the chlorination stage, the use of O_2 and hydrogen peroxide (H_2O_2) in the first caustic extraction stage also reduces AOX generation by minimizing the bleach chemical charge for the subsequent stage (s) [8].

In this chapter, the generation of effluent pollution load, i.e. biochemical oxygen demand (BOD), chemical oxygen demand (COD), color, AOX, chlorophenolics, and cRFA, by different pulp bleaching sequences (D/CED, DED, DE_PD, and ODED) has been studied. Additionally, the effect of bleaching on pulp characteristics, i.e. viscosity and strength properties, has also been investigated. The mixed hardwood kraft pulp was bleached with D/CED, DED, DE_PD, and ODED sequences and the effluents generated (individual stage) have been characterized in terms of BOD, COD, color, AOX, chlorophenolics, and cRFA.

3.2 PULP BLEACHING TECHNOLOGY MODIFICATION

3.2.1 O_2 delignification

O_2 delignification can be defined as a process using O_2 under alkaline conditions for removing a substantial amount of lignin in unbleached pulp [1]. O_2 is poorly selective at high degree of delignification and may lead to reduction in pulp quality and yield, if used extensively, by carbohydrate degradation [9]. Hence, pulp delignification by O_2 is limited to about 40-50% of the residual lignin [10-12]. The carbohydrate degradation is caused by active O_2 species and chain type reactions initiated by $HOO^{\bullet}$, $O_2^{\bullet -}$, and $HO^{\bullet}$, which are generated through the reduction of O_2 species and the lignin reactions [13-15]. The delignification selectivity in O_2 delignification may be improved by the use of catalysts and activators, e.g. magnesium salts, polyoxometalates [10, 16], metalloporphyrins [17], and other transition metal based catalysts [18].

Free phenolic OH group gets ionized under alkaline conditions and furnish high electron density for initiating reaction with relatively weakly oxidizing O_2. The ionized phenolic group is converted to phenoxy radical by loss of one electron to O_2, $O_2^{\bullet -}$ or $HOO^{\bullet}$. The phenoxy radical is a resonance hybrid of the structures depending on position of the odd electron, i.e. at phenolic oxygen, any of the carbon atoms of aromatic ring or β-carbon atom of side chain. All these positions are potential sites for conversion to hydroperoxide intermediate (Figure 3.1) which can undergo an intra-molecular nucleophilic reaction at an adjacent site to finally produce oxirane, muconic acid, and carbonyl structures (Figure 3.2). All these reactions lead to lignin fragmentation and introduction of hydrophilic groups and thus increase the solubility of lignin in alkaline medium [1].

A lower kappa number after O_2 delignification stage results in a lower oxidizing chemicals charge needed to delignify the pulp to achieve the target brightness. Furthermore, O_2 delignification contributes to a corresponding decrease in AOX, BOD, COD, and color in the bleach plant effluent [1, 19]. Application of O_2 delignification has been reported to offset the total bleaching costs by 20% on an average [7, 20]. O_2 stage effluent can be recycled to the recovery system which decreases the environmental impact of bleach plant [1].

3.2.2 Replacement of Cl_2 by ClO_2

Industrial Cl_2 substitution with ClO_2 (5-10%) was at first only a means of protecting pulp strength [1]. But now mills have switched to 100% substitution to reduce both the amount and degree of chlorinated compounds generated during pulp bleaching [21]. The highest delignification efficiency occurs at about 50% replacement of Cl_2 with ClO_2 and when ClO_2 is applied prior to Cl_2 addition. At 100% substitution, ClO_2 is much less effective, often resulting in higher lignin content after the CE stages and lower final brightness. But, it has the advantages of pulp strength protection, resin content reduction, and decreased NaOH consumption in the first extraction stage [22].

ClO_2 is a much stronger oxidant having 5 times the oxidation power of Cl_2 per chlorine atom [21]. Muconic acid esters are formed by the oxidation of lignin [23] and ClO_2 is reduced to chlorite ion (ClO_2^-) and hypochlorous acid (HOCl). ClO_2^- ions decompose in the acid medium to reform ClO_2 and Cl^- ion or they react with HOCl to form chlorate ion (ClO_3^-) [24]. HOCl may react with organic material to form chlorinated organics. This reaction may be direct or it may involve the formation of Cl_2 which can exist in equilibrium with HOCl depending on pH [25]. HOCl reacts with the lignin to produce chlorohydrins. Chlorine from chlorohydrins is easily eliminated during subsequent alkaline extraction and less chlorinated organics are formed (Figure 3.3).

ClO_2 bleaching effluents present lower environmental load as compared to Cl_2 bleaching [26]. Increasing ClO_2 substitution from 45 to 60 to 100% of chlorine demand resulted in decreased AOX (40-60%), color (35%), and chlorinated phenolics (95%) in the effluent [27, 28]. ECF bleaching generates organically bound chlorine but only one-fifth of those with same amount of the elemental chlorine [29]. Pryke [30] and Singh [31] reported decrease in effluent toxicity with increase in ClO_2 substitution.

3.2.3 H_2O_2 reinforced alkaline extraction

H_2O_2 has been recognized as an environmentally friendly and strong oxidizing agent for bleaching [32-34]. H_2O_2 can be used in combination with NaOH to reinforce an alkaline extraction (E_P) stage, or as a delignification and bleaching agent to decrease pulp kappa number and increase brightness and brightness stability [34, 35]. It is generally believed that not only the hydroperoxide anion (OOH^-), but also $OH^\bullet$ radicals generated by H_2O_2 decomposition caused by transition metals play a role in the degradation of pulp components during alkaline H_2O_2 bleaching [23, 33, 36, 37]. The OOH^- anion, a strong nucleophile, converts electron rich chromophores, i.e. unsaturated aldehydes and ketones, and phenolic ring-conjugated ethylenic or carbonyl groups, to their non-chromophoric counterparts during bleaching. The lignin reactions with H_2O_2 are not reversible and result in the permanent removal of most of the chromophoric groups present in the lignin molecule [33, 38].

$$H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O \qquad (3.1)$$

$$H_2O_2 + HO_2^- \rightarrow OH^\bullet + O_2^{\bullet -} + H_2O \qquad (3.2)$$

$$O_2^{\bullet -} + OH^\bullet \rightarrow O_2^\bullet + OH^- \qquad (3.3)$$

$$H_2O_2 + M^{n+} \rightarrow M^{(n+1)+} + OH^\bullet + OH^- \qquad (3.4)$$

$$HO_2^- + M^{(n+1)+} \rightarrow M^{n+} + O_2^{\bullet -} + H^+ \qquad (3.5)$$

H_2O_2 addition in E stage decreases the lignin content further by additional oxidation and thus allows the kappa factor for a given kappa target to be lowered. H_2O_2 in E_1 stage results in better delignification, higher brightness, and lower demand for ClO_2. E_2 stage application of moderate amount of H_2O_2 results in cost effective substitution of ClO_2, higher brightness stability, and lower level of chlorinated compounds (AOX). The pulp brightness in E stage increases between 75 and 80% of the initial brightness, depending on the amount of H_2O_2 added [39]. Some mills using only ClO_2 in the first stage have had difficulty in reaching high brightness (90% ISO), the addition of H_2O_2 to E stage has helped to overcome this problem [40, 41]. The effluent color improves from dark brown to light brown by H_2O_2 use in E stage [39] and AOX released to receiving waters decreases because less chlorine is required in the first bleaching stage [42].

3.3 RESULTS AND DISCUSSION

3.3.1 O_2 delignification

O_2 delignification was targeted for 40-50% reduction in pulp kappa number with minimum drop in the pulp viscosity. The optimization of the alkali charge (NaOH) during O_2 stage was carried out by varying alkali dose under optimum conditions of O_2, pulp consistency, retention time, temperature, and $MgSO_4.7H_2O$ (Table 3.1). Figure 3.4 depicts the effect of NaOH charge during O_2 delignification on pulp kappa number, viscosity, and brightness. As NaOH charge is increased there is a decrease in the pulp kappa number but the pulp viscosity drops. These findings are in concordance with those reported earlier by other authors [43]. Hence optimization of NaOH charge is necessary because excess of NaOH results in low quality pulp by viscosity loss. As is evident from Figure 3.4 and Table 3.1, at a NaOH charge of 10 kg/t O.D. pulp, kappa number drops to 9.1 from the initial value of 15 giving a reduction of 39% which is below the target reduction of 40-50%. So, higher doses of NaOH, i.e. 20 and 30 kg/t O.D. pulp, were tried. At 20 kg/t O.D. pulp of NaOH charge, pulp kappa number reduced to 8.3 and viscosity to 12.2 cP. So, it is selected as optimum dose as almost 45% kappa number reduction is achieved with 12% viscosity drop. At higher NaOH dose (30 kg/t O.D. pulp), the viscosity drops by 19% and kappa number by 51%, so a NaOH dose of 20 kg/t O.D. pulp was selected as optimum for generating oxygen delignified pulp. The pulp brightness increased as NaOH charge was increased. A brightness of 49% ISO was obtained at 20 kg/t O.D. pulp of NaOH charge.

3.3.2 Chemical consumption for target brightness (87% ISO)

The pulp was bleached to 87% ISO target brightness using D/CED, DED, DE_PD, and ODED sequences. The pulp bleaching conditions for different stages of various pulp bleaching sequences are mentioned in Table 2.1 and 2.2. The kappa factor (KF) was varied (0.28-0.35) for attaining 87% ISO target brightness during different bleaching sequences. For DED sequence a KF of 0.35 was found to be optimum while for other sequences, KF value of 0.3 was found optimum for attaining the same target brightness. Figure 3.5 illustrates the effect of KF on pulp brightness during different bleaching sequences for achieving 87% ISO target brightness. Table 3.2 and Figure 3.6 show quantity of different chemicals charged for attaining 87% ISO target brightness and chemicals consumption during different pulp bleaching sequences, respectively.

The total active chlorine consumption followed the order: DED > D/CED and DE$_P$D > ODED. The bleach (aCl$^-$) chemical saving by use of O_2 delignification is 53% as compared to DED sequence and 45% as compared to D/CED and DE$_P$D sequences. While in case of D/CED and DE$_P$D sequences, 14% bleach chemical (aCl$^-$) savings was observed as compared to DED sequence. The alkali (NaOH) savings of 30% was achieved by DED, DE$_P$D, and ODED sequences as compared to D/CED sequence. ECF bleaching sequences have been reported to reduce the alkaline charge [22].

3.3.3 Pulp strength properties

The pulp after bleaching with different bleaching sequences was beaten to the same CSF (300 mL ± 20) in a PFI mill before making hand sheets for testing mechanical strength properties. The pulp beating is carried out to improve runability-strength properties of paper and bonding ability of fibers [44]. Figure 3.7 (a-d) shows effect of different bleaching sequences on pulp tear index, tensile index, burst index, and viscosity. The pulp tear index improved after all bleaching sequences. Highest increase was observed for DE$_P$D bleached pulp followed by ODED, DED, and D/CED sequences. Slight decrease in pulp tensile index was observed after bleaching. DE$_P$D bleached pulp was observed to be having highest tensile index followed by ODED, DED, and D/CED sequences. Pulp burst index also decreased after bleaching. Lowest decrease was observed for DE$_P$D sequence followed by ODED, DED, and D/CED sequences. Small decrease in pulp viscosity was observed after bleaching. Highest drop in pulp viscosity was observed for D/CED bleached pulps. For DE$_P$D bleached pulps viscosity dropped to the least extent followed by ODED, DED, and D/CED sequences. After O_2 delignification stage tear index improved, while tensile index, burst index, and pulp viscosity decreased. The pulp with somewhat improved strength properties was obtained after ECF bleaching sequences as compared to D/CED sequence. The pulp properties have been reported to be preserved during ECF bleaching [22].

3.3.4 Pollution load generation in effluent

3.3.4.1 General parameters

Table 3.3 and Figure 3.8 (a-d) depicts BOD, COD, color, and AOX generation during different bleaching stages and total quantity, respectively, for D/CED, DED, DE$_P$D, and ODED sequences. ODED sequence effluents were found to be having lowest pollution load as compared to other sequences. This is due to the reduction (45%) of initial kappa number of the pulp after O_2 delignification stage, which in turn reduces the active chlorine multiple required for the next bleaching stages and environmental load [1]. The major pollution load came from first two bleaching (D/C or D_1 and E or E_P) stages for all the bleaching sequences. During kraft pulp bleaching, a significant amount of organic matter is dissolved in the first two bleaching stages i.e. chlorination and alkaline extraction [45].

DED sequence effluents presented high BOD and COD load as compared to D/CED, DE_PD, and ODED sequences (Figure 3.8 a and b). This is due to the requirement of higher chemical charge (KF 0.35) in DED sequence for achieving 87% ISO target brightness as compared to other sequences. Tsai et al. [45] also reported similar findings that COD generation increases as KF increases. At 100% substitution, ClO_2 is much less effective often resulting in higher CE lignin content and lower final brightness, hence higher bleach chemical charge is needed [22]. The highest color was generated in D/CED sequence (50% ClO_2 and 50% Cl_2) effluents as compared to DED, DE_PD, and ODED sequences (100% ClO_2) (Figure 3.8 c). The literature reports that effluent color decreases with increasing ClO_2 substitution for Cl_2 [45, 46]. COD and color load of the effluents is also a function of the kappa number of the unbleached pulp and KF, the kappa number being the variable having the highest impact. The kappa number decrease of the unbleached pulp decreases the amount of COD, color, and AOX generation during pulp bleaching at high ClO_2 substitution levels [45].

The highest amount of AOX was generated in D/CED sequence effluents as compared to DED, DE_PD, and ODED sequences (Figure 3.8 d). For DED sequence higher AOX was generated as compared to DE_PD and ODED sequences. This is due to the requirement of higher KF for achieving the same target brightness. For ODED sequence lowest AOX was generated due to use of O_2 stage. H_2O_2 reinforced alkaline extraction in DE_PD sequence reduced the requirement of active chlorine multiple (KF 0.30) hence lower AOX was generated as compared to DED sequence. The effluent AOX loadings increase with an increase in KF but decrease with an increase in ClO_2 substitution and decrease in initial kappa number [45, 46].

3.3.4.2 Chlorophenolics generation

During pulp chlorination, lignin is chlorinated and breaks down to simpler chlorophenolic compounds which have low solubility in acidic conditions of D/C or D_1 stage and are solubilized in alkaline condition of E or E_P stage [47]. Chlorination and alkaline extraction stages often account for the largest fraction of chloroorganics in the bleach plant effluent [45, 48]. Gas chromatography (GC) - Mass spectrometry (MS) analysis facilitated identification of six types of chlorophenolic compounds in the pulp bleaching effluents in terms of chemical family, i.e. chlorophenols (CP), chloroguaiacols (CG), chlorocatechols (CC), chlorovanillin (CV), chlorosyringol (CS), and chlorosyringaldehyde (CSA). Similar chlorophenolic compounds have been reported to be present in the pulp bleaching effluents by other authors [3, 49]. Gas chromatogram of a laboratory prepared mixture of 26 reference chlorophenolic compounds (acetyl derivatives) is shown in Figure 3.9. The corresponding retention time (RT), base peak mass/charge (m/z) ratio, and extraction efficiency (EE) values are given in Table 3.4. The structure of various chlorophenolic compounds by chemical family is depicted in Figure 3.10.

(a) Chlorophenolics generation during D/CED sequence

For D/C stage effluent, among the identified chlorophenolics, CP (41%), CC (28%), CG (17%), and CS (10%) were the major contributors. CSA and CV were detected in small quantity (<3%) (Figure 3.13 a). CP and CC together contributed 69% of the total chlorophenolics. Among CP, the major contribution came from 2,4,5-TCP followed by 2,5-DCP, 2,4-DCP, 3-CP, PCP, and 4-CP. Other CP were detected in small quantities (<5 mg/t O.D. pulp). About 92.6% contribution came from 2,4,5-TCP, 2,5-DCP, and 2,4-DCP. Among CG, the highest contribution came from Tet-CG followed by 3,4,5-TCG, 4,6-DCG, 4,5-DCG, 4,5,6-TCG, 3,4,6-TCG, and 4-CG. About 79% is contributed by Tet-CG, 3,4,5-TCG, 4,6-DCG, and 4,5-DCG. Out of three CC compounds detected, 3,6-DCC contributed to the highest extent followed by 3,5-DCC and Tet-CC. Among other chlorophenolics, significant quantities of TCS, 2,6-DCSA, and 5,6-DCV were detected. The total generation of chlorophenolic compounds was 2126 mg/t O.D. pulp (Table 3.5). The highest contribution came from dichlorophenols (DCP) (58%) followed by trichlorophenols (TCP) (33%), and tetrachlorophenols (Tet-CP) (6%). Monochlorophenols (MCP) and pentachlorophenols (PCP) contributed to small extent (<2%) (Figure 3.13 e).

For E stage effluent, among the identified chlorophenolics, the significant contribution came from CP (34%) followed by CG (33%), CS (18%), CSA (7%), CC (6%), and CV (2%) (Figure 3.13 b). Among CP, the major contribution came from 2,4,5-TCP followed by 2,5-DCP, 2,4-DCP, 3-CP, 4-CP, and 2,3,4-TCP. Other CP were detected in small quantities (<5 mg/t O.D. pulp). About 94% contribution came from 2,4,5-TCP, 2,5-DCP, and 2,4-DCP. Among CG, the highest contribution came from 4,6-DCG followed by 3,4,5-TCG, 4,5-DCG, Tet-CG, 3,4,6-TCG, 4,5,6-TCG, and 4-CG. About 87% is contributed by 4,6-DCG, 3,4,5-TCG, 4,5-DCG, and Tet-CG. Among CC, highest contribution came from 3,6-DCC followed by 3,5-DCC and Tet-CC. Among remaining chlorophenolics, significant quantities of TCS, 2,6-DCSA, and 5,6-DCV were detected. The total generation of chlorophenolic compounds was 4211 mg/t O.D. pulp (Table 3.5). The highest contribution came from DCP (48%) followed by TCP (45%), Tet-CP (5%), and MCP (2%). PCP was detected in trace amount (0.06%) (Figure 3.13 f).

For D stage effluent, among the identified chlorophenolics, the major contribution came from CG (50%) followed by CP (35%), CS (13%), and CC (2%). CSA and CV were not detected (Figure 3.13 c). Among the identified CP, the major contribution came from 2,4,5-TCP followed by 2,5-DCP, 2,3,5-TCP, and 3-CP. Other CP were detected in trace amounts (< 0.7 mg/t O.D. pulp). 2,6-DCP, 3,4-DCP, 2,4,6-TCP, and PCP were not detected. 2,4,5-TCP alone contributed about 62%. Among CG, the highest contribution came from 4-CG followed by 4,5-DCG, Tet-CG, 3,4,6-TCG, and 4,6-DCG. About 68% was contributed by 4-CG and 4,5-DCG. Among remaining chlorophenolics, only Tet-CC and TCS were detected. The total generation of chlorophenolic compounds was 47 mg/t O.D. pulp (Table 3.5). The highest contribution came from TCP (46%) followed by DCP (24%), MCP (20%), and Tet-CP (10%). PCP was not detected (Figure 3.13 g). Figure 3.13 (d) and (h) shows the proportion of chlorophenolics out of the total quantity generated by D/CED sequence. Major contribution came from CP (37%) followed by CG (28%), CS (15%), CC (13%), CSA (6%), and CV (1%). DCP were generated to the highest extent (52%) followed by TCP (41%), Tet-CP (5%), MCP (2%), and PCP (0.04%).

(b) Chlorophenolics generation during DED sequence

For D_1 stage effluent, among the identified chlorophenolics, highest contribution came from CG (60%) followed by CC (27%), CP (9%), and CSA (3%). CS and CV were present in trace amounts (<0.5%). CG and CC together contributed 87% of the total chlorophenolics

(Figure 3.14 a). Among CP, the major contribution came from 3-CP followed by 2,5-DCP and 2,3,5-TCP, 4-CP, 2,4,5-TCP, 2,3,4-TCP, PCP, 2,6-DCP and 2,3,6-TCP. Other CP were detected in small quantities (<1.6 mg/t O.D. pulp). About 61% contribution came from 3-CP, 2,5-DCP, 2,3,5-TCP, and 4-CP. Among CG, the highest contribution came from 4,5-DCG followed by 4-CG, 4,6-DCG, Tet-CG, and 3,4,6-TCG. About 97% is contributed by 4,5-DCG and 4-CG. Other CG were present in small quantities (<0.9 mg/t O.D. pulp). Among CC, the highest contribution came from 3,6-DCC followed by 3,5-DCC and Tet-CC. Among other chlorophenolics, significant contribution came from 2,6-DCSA followed by 5,6-DCV and TCS. The total generation of chlorophenolic compounds was 398 mg/t O.D. pulp (Table 3.6). The highest contribution came from DCP (78%) followed by MCP (14%), TCP (4%), Tet-CP (3%), and PCP (1%) (Figure 3.14 e).

For E stage effluent, among the identified chlorophenolics, highest contribution came from CG (63%) followed by CP (19%), CC (13%), and CSA (5%). CV was detected in trace amount (0.3%). CS was not detected. CG and CP together contributed 82% of the total chlorophenolics (Figure 3.14 b). Among CP, the major contribution came from 3-CP followed by 4-CP, 2,5-DCP, 2,4,5-TCP, PCP, 2,3,4-TCP, and 3,4-DCP. Other CP were detected in small quantities (<0.7 mg/t O.D. pulp). About 90% contribution came from 3-CP and 4-CP. 2,3,6-TCP and 2,3,5-TCP were not detected. Among CG, the highest contribution came from 4,5-DCG followed by 4-CG, 4,5,6-TCG, Tet-CG, 4,6-DCG, and 3,4,6-TCG. 3,4,5-TCG was detected in trace quantity (0.8 mg/t O.D. pulp). About 97% is contributed by 4,5-DCG and 4-CG. Among CC, the highest contribution came from 3,6-DCC followed by 3,5-DCC and Tet-CC. Among other chlorophenolics, significant contribution came from 2,6-DCSA and 5,6-DCV. TCS was not detected. The total generation of chlorophenolic compounds was 656 mg/t O.D. pulp (Table 3.6). The highest contribution came from DCP (49%) and MCP (48%). TCP, Tet-CP, and PCP were detected in small quantity (<2%) (Figure 3.14 f).

For D_2 stage effluent, among the identified chlorophenolics, the highest contribution came from CG (46%) followed by CC (39%) and CP (15%). CSA, CS, and CV were not detected (Figure 3.14 c). Among CP, the major contribution came from 2,4,5-TCP and 3,4-DCP i.e. 44%. Other CP were detected in small quantities (<0.9 mg/t O.D. pulp). 2,3,6-TCP, 2,3,5-TCP, 2,4,6-TCP, and PCP were not detected. Among CG, out of three identified compounds the highest contribution came from 4,5-DCG followed by 4-CG and 4,6-DCG. Among CC, the major contribution came from 3,6-DCC followed by 3,5-DCC. Other chlorophenolics were not identified. The total generation of chlorophenolic compounds was 50 mg/t O.D. pulp (Table 3.6). The highest contribution came from DCP (72%) followed by MCP (22%) and TCP (6%). Tet-CP and PCP were not detected (Figure 3.14 g). Figure 3.14 (d) and (h) shows the proportion of chlorophenolics out of the total quantity generated by DED sequence. Major contribution came from CG (62%) followed by CC (19%), CP (15%), CSA (4%), CV (0.4%), and CS (0.2%). DCP were generated to the highest extent (61%) followed by MCP (34%), TCP (3%), Tet-CP (2%), and PCP (0.4%). The generation of chlorophenolics was reduced by about 81 and 84% in D_1 and E stage effluents, respectively, while the total generation of chlorophenolics was reduced by 83% as compared to D/CED sequence.

(c) Chlorophenolics generation during DE_PD sequence

For D_1 stage effluent, among the identified chlorophenolics, the highest contribution came from CG (62%) followed by CC (32%) and CP (6%). CSA, CS, and CV were not detected. CG and CC together contributed 94% of the total chlorophenolics (Figure 3.15 a). Among CP, the major contribution came from 2,5-DCP followed by 3-CP, 2,4,5-TCP, 2,3,4-TCP, 2,6-DCP, 4-CP and 3,4-DCP. 2,4-DCP was detected in small quantity (0.4 mg/t O.D. pulp). About 63% contribution came from 2,5-DCP, 3-CP, and 2,4,5-TCP. 2,3-DCP, 2,3,6-TCP, 2,3,5-TCP, 2,4,6-TCP, and PCP were not detected. Among CG, the highest contribution came from 4,5-DCG and 4-CG. The trace quantities of 4,6-DCG and 3,4,5-TCG were identified (<0.8 mg/t O.D. pulp). 3,4,6-TCG, 4,5,6-TCG, and Tet-CG were not detected. Among other chlorophenolics only Tet-CC was detected. The total generation of chlorophenolic compounds was 278 mg/t O.D. pulp (Table 3.7). The highest contribution came from DCP (77%) and MCP (18%). TCP and Tet-CP contributed to smaller extent (<3%). PCP was not detected (Figure 3.15 e).

For E_P stage effluent, among the identified chlorophenolics, highest contribution came from CG (80%) and CP (16%). CSA, CC, and CV were detected in small amounts (<2%). CS was not detected. CG and CP together contributed 96% of the total chlorophenolics (Figure 3.15 b). Among CP, the major contribution came from 3-CP followed by 2,5-DCP, 2,4,5-TCP, 2,3,4-TCP, and 3,4-DCP. 4-CP and 2,4-DCP were detected in small quantities (0.6 mg/t O.D. pulp).

2,6-DCP, 2,3-DCP, 2,3,6-TCP, 2,3,5-TCP, 2,4,6-TCP, and PCP were not detected. About 94% contribution came from 3-CP, 2,5-DCP, and 2,4,5-TCP. Among CG, the highest contribution came from 4,5-DCG followed by 4-CG, 4,6-DCG, and 4,5,6-TCG. 3,4,6-TCG, 3,4,5-TCG, and Tet-CG were not detected. About 99% is contributed by 4,5-DCG and 4-CG. Among other chlorophenolics, significant contribution came from 2,6-DCSA, Tet-CC, and 5,6-DCV. TCS was not detected. The total generation of chlorophenolic compounds was 393 mg/t O.D. pulp (Table 3.7). The highest contribution came from DCP (54%) and MCP (44%). TCP and Tet-CP were detected in small amounts (<1%). PCP was not detected (Figure 3.15 f).

For D_2 stage effluent, among the identified chlorophenolics, the highest contribution came from CG (68%) followed by CP (26%), CC (4%), and CSA (2%). CS and CV were not detected (Figure 3.15 c). Among CP, the major contribution came from 2,4,5-TCP, 2,5-DCP, and 3,4-DCP (67%). 3-CP, 2,3,4-TCP, 4-CP, and 2,4-DCP were detected in small quantities (< 0.9 mg/t O.D. pulp). 2,6-DCP, 2,3-DCP, 2,3,6-TCP, 2,3,5-TCP, 2,4,6-TCP, and PCP were not detected. Among other chlorophenolics, 4,5-DCG, Tet-CC, and 2,6-DCSA were identified. The total generation of chlorophenolic compounds was 21 mg/t O.D. pulp (Table 3.7). The highest contribution came from DCP (80%) followed by TCP (11%), MCP (5%), and Tet-CP (4%). PCP was not detected (Figure 3.15 g). Figure 3.15 (d) and (h) shows the proportion of chlorophenolics out of the total quantity generated by DE_PD sequence. Major contribution came from CG (72%) followed by CC (14%), CP (13), CSA (1%), and CV (0.3%). CS was not detected. DCP were generated to the highest extent (64%) followed by MCP (32%), TCP and Tet-CP (2%). PCP was not detected. The generation of chlorophenolics was reduced by about 87, 91, and 55%, respectively in D_1, E_P, and D_2 stage effluents, respectively, while the total generation of chlorophenolics was reduced by 89% as compared to D/CED sequence.

(d) Chlorophenolics generation during ODED sequence

For D_1 stage effluent, among the identified chlorophenolics, the highest contribution came from CC (63%) followed by CP (17%), CG (14%), CV and CSA (3%). CS was not detected. CC and CP together contributed 80% of the total chlorophenolics (Figure 3.16 a). Among CP, the major contribution came from 2,4,5-TCP followed by 3-CP and 2,5-DCP, 3,4-DCP, and, 2,3,4-TCP. Other CP were detected in small quantities (< 0.7 mg/t O.D. pulp). 2,3-DCP, 2,3,6-TCP, 2,3,5-TCP, and PCP were not detected. About 82% contribution came from

2,4,5-TCP, 2,5-DCP, and 3-CP. Among CG, the highest contribution came from 4,5-DCG, 4-CG, and 3,4,6-TCG. The trace quantities of 3,4,5-TCG and 4,6-DCG were detected (< 0.8 mg/t O.D. pulp). 4,5,6-TCG and Tet-CG were not detected. Among CC, the highest contribution came from 3,6-DCC followed by 3,5-DCC and Tet-CC. Among other chlorophenolics, 5,6-DCV and 2,6-DCSA were detected. The total generation of chlorophenolic compounds was 154 mg/t O.D. pulp (Table 3.8). The highest contribution came from DCP (76%) followed by TCP (14%), MCP (6%), and Tet-CP (4%). PCP was not detected (Figure 3.16 e).

For E stage effluent, among the identified chlorophenolics, the highest contribution came from CG (81%) and CP (12%). CC, CV, CSA, and CS were detected in small amounts (< 2%). CG and CP together contributed 93% of the total chlorophenolics (Figure 3.16 b). Among CP, the major contribution came from 2,4,5-TCP followed by 2,5-DCP, 2,3,5-TCP, 2,3,4-TCP, 3,4-DCP, 3-CP, and 2,3,6-TCP. 4-CP, 2,6-DCP, 2,4-DCP, and 2,3-DCP were detected in small quantities (<0.9 mg/t O.D. pulp). 2,4,6-TCP and PCP were not detected. About 71% contribution came from 2,4,5-TCP, 2,5-DCP, and 2,3,5-TCP. Among CG, the highest contribution came from 4,5-DCG followed by 4-CG and 4,6-DCG. Other CG were not detected. Among other chlorophenolics, the highest contributed came from 5,6-DCV followed by 2,6-DCSA, Tet-CC, and TCS. The total generation of chlorophenolic compounds was 264 mg/t O.D. pulp (Table 3.8). The highest contribution came from DCP (70%) followed by MCP (18%), TCP (10%), and Tet-CP (2%) (Figure 3.16 f).

For D_2 stage effluent, only CG (64%) and CP (36%) were detected (Figure 3.16 c). Among CP, the major contribution came from 3-CP and 2,3,4-TCP (60%). 2,5-DCP, 2,4,5-TCP, 4-CP, 2,6-DCP, and 2,4-DCP were detected in small amounts (<0.7 mg/t O.D. pulp). Other CP were not detected. Among CG, the highest contribution came from 4-CG followed by 4,5-DCG and 4,6-DCG. 3,4,5-TCG and 4,5,6-TCG were detected in small quantities (<0.8 mg/t O.D. pulp). Other CG and chlorophenolics were not detected. The total generation of chlorophenolic compounds was 13 mg/t O.D. pulp (Table 3.8). The highest contribution came from MCP (42%) followed by DCP (36%) and TCP (22%). Tet-CP and PCP were not detected (Figure 3.16 g). Figure 3.16 (d) and (h) shows the proportion of chlorophenolics out of the total quantity generated by ODED sequence. Major contribution came from CG (57%) followed by CC (23%), CP (15%), CV and CSA (2%), and CS (1%). DCP were generated to the highest extent

(71%) followed by MCP (15%), TCP (12%), and Tet-CP (2%). PCP was not detected. The generation of chlorophenolics was reduced by about 93, 94, and 72% in D_1, E, and D_2 stage effluents, respectively, while the total generation of chlorophenolics was reduced by 93% as compared to D/CED sequence.

The highest amount of chlorophenolics was generated in D/CED sequence effluents as compared to DED, DE_PD, and ODED sequences. The total concentration of chlorophenolics was found to be very low at 100% ClO_2 substitution (Tables 3.5-3.8 and Figure 3.11 a-f). These findings are in good agreement with those reported earlier that concentration of chlorophenolics in the bleaching effluents decreases as ClO_2 substitution increases [45]. The chlorophenolics detected in DED, DE_PD, and ODED sequences are due to the generation of Cl_2 and HOCl during the initial ClO_2 reactions with some lignin structural units [50]. The generation of polychlorinated phenolic compounds decreased sharply by DED, DE_PD, and ODED sequences as compared to D/CED sequence (Figures 3.12 a-e). These results are supported by the literature that the polychlorinated phenolic compounds generation decreases at or below detection limit at 100% ClO_2 substitution [51].

CP and CG were generated in higher amount for D/CED sequence effluents followed by DED, DE_PD, and ODED sequences. The highest amount of CC and CSA was generated in D/CED sequence effluents followed by DED, ODED, and DE_PD sequences. The relatively higher concentration of CC was generated for O_2 delignified pulp as compared to DE_PD. The oxidative demethylation during O_2 bleaching leaves catechol moities on the residual lignins that are particularly susceptible to chlorination. Higher amount of CV was generated for D/CED sequence effluents followed by ODED, DED, and DE_PD sequences. CS was generated to higher extent for D/CED sequence effluents followed by ODED and DED sequences. It was not detected in DE_PD sequence effluents (Figures 3.11 a-f). The results are similar as reported earlier by other workers that CC, CG, and CS are the byproducts of pulp bleaching with chlorine [52].

Higher amount of chlorophenolics was generated in DED sequence effluents as compared to DE_PD and ODED sequences due to requirement of higher KF. MCP were generated in the higher amount in DED sequence followed by DE_PD > D/CED > ODED sequences. DCP and Tet-CP were generated in the higher amount in D/CED sequence followed by DED > DE$_P$D > ODED sequences. TCP were generated in the higher amount in D/CED sequence followed by ODED > DED > DE$_P$D sequences. Few polychlorinated phenolics are produced at low KF and their concentration increase as KF increases [29]. PCP, the most toxic of the group, was detected only in D/CED and DED sequence effluents (Figure 3.12 a-e). PCP generation may be due to the use of elemental chlorine and high KF requirement in D/CED and DED sequences, respectively. ClO_2 substitution for Cl_2 highly reduces the chloroorganics generation [27-29]. For ODED sequence lower amount of chlorophenolics was generated due to reduction of initial kappa number of the pulp. In DE$_P$D sequence use of H_2O_2 decreased requirement of chemical charge which decreased quantity of chlorophenolics in the effluent as compared to DED sequence. These findings are in good agreement with the literature [39]. The chlorophenolics effluent loading increases with increasing KF, decreasing ClO_2 substitution for Cl_2, and increased kappa number of the unbleached pulp.

The lowest chlorophenolics generated for ODED sequence effluents followed by DE$_P$D < DED < D/CED sequences is in agreement with the results of many authors [49, 53, 54]. Cl_2 application in D/CED sequence generated higher amount of chloroorganics. Axegard et al. [55] reported that the generation of highly halogenated phenolic compounds decreases at high levels of ClO_2 substitution. ECF bleaching processes generates only 10-20% of the chlorinated compounds as found in chlorine based bleaching effluents [56]. In accordance with the above the generation of DCP was reduced by 80, 87, and 91%, respectively, in DED, DE$_P$D, and ODED sequences as compared to D/CED sequence. TCP generation was reduced by 99, 99.5, and 98% in DED, DE$_P$D, and ODED sequences, respectively, as compared to D/CED sequence. While, Tet-CP generation was reduced by 94, 96, and 97% in DED, DE$_P$D, and ODED sequences, respectively, as compared to D/CED sequence. PCP was not generated in DE$_P$D and ODED sequence effluents. In DED sequence PCP generation was reduced by about 72% as compared to D/CED sequence. CP, CC, CS, and CSA generation was reduced in the range of 93-97, 75-88, 99.7-99.8, and 98-99.9% in DED, DE$_P$D, and ODED sequences, respectively, as compared to D/CED sequence. These findings are in accordance with those reported by Liebergott et al. [57] that CC and CG generation decreases drastically by ClO_2 substitution. CG and CV generation was reduced in the range of 62-97% and 91-98%by DED, DE$_P$D, and ODED sequences, respectively, as compared to D/CED sequence. Berry et al. [58] reported similar findings that CV and CG are formed to lesser extent for ClO_2 bleaching effluents. The findings are on the similar trend as earlier reported that AOX and toxicity are lower for ECF bleaching effluents [55] due to decrease in generation of chlorophenolics and their lower degree of chlorination [59]. Based on the above findings, the generation of chlorophenolics during different bleaching sequences can be correlated as mentioned below:

$$Chlorophenolics\ (DED) = 0.17 \times D/CED\ chlorophenolics \tag{3.6}$$

$$Chlorophenolics\ (DE_pD) = 0.12 \times D/CED\ or\ 0.63 \times DED\ chlorophenolics \tag{3.7}$$

$$Chlorophenolics\ (ODED) = 0.07 \times D/CED\ or\ 0.39 \times DED\ or\ 0.62 \times DE_pD\ chlorophenolics \tag{3.8}$$

3.3.4.3 Chloro-resin and fatty acids (cRFA) generation

Three cRFA compounds, i.e. chlorodehydroabietic acid (CDAA), 12,14-dichlorodehydroabietic acid (DCDAA), and 9,10,12,13-tetrachlorostearic acid (TCSA) were detected in the effluents of D/CED, DED, DE_PD, and ODED sequences. Gas chromatogram of a laboratory prepared mixture of four reference cRFA compounds (methyl derivatives) separated on GC is shown in Figure 3.17. The corresponding RT, response factor (RF), and EE values are given in Table 3.9. The structure of various cRFA compounds is depicted in Figure 3.18. The quantity of cRFA generated during different stages of D/CED, DED, DE_PD, and ODED sequences is mentioned in Table 3.10. Figures 3.19 shows proportion (%) of cRFA generated during different stages of D/CED and DED sequences while the same for DE_PD and ODED sequences is depicted in Figure 3.20. Higher quantity of cRFA was generated in E stage effluents of all bleaching sequences as compared to D_1 and D_2 stages. This may be due to the higher solubility of cRFA in the alkaline media of E stage than acidic media of D stage. The highest quantity of cRFA was generated in D/CED sequence effluents followed by DED, DE_PD, and ODED sequences (Table 3.10). Table 3.11 summarizes quantity of cRFA in terms of chloro-resin acids (cRA) and chloro-fatty acids (cFA) generated during different stages of D/CED, DED, DE_PD, and ODED sequences. cRA were generated in higher amount as compared to cFA. cFA were not detected in ODED sequence effluents.

(a) cRFA generation during D/CED sequence

For D/C stage of D/CED sequence the highest contribution came from CDAA (57%) followed by DCDAA (33%) and TCSA (10%). For E stage the highest proportion came from CDAA (47%) followed by DCDAA (31%) and TCSA (22%). In D stage effluent only CDAA

(58%) and DCDAA (42%) were identified (Figure 3.19 a-c). About 3 times higher cRFA were generated in E stage effluent as compared to D/C stage. The highest quantity of cRFA was generated in E stage effluent followed by D/C and D stages (Table 3.10). Out of the total cRFA generated the highest proportion came from CDAA (50%) followed by DCDAA (32%) and TCSA (18%) (Figure 3.19 d).

(b) cRFA generation during DED sequence

For D_1 stage of DED sequence the highest contribution came from CDAA (66%) followed by DCDAA (22%) and TCSA (12%). For E stage, the highest proportion came from CDAA (53%) followed by DCDAA (38%) and TCSA (9%). In D_2 stage effluent only CDAA (56%) and DCDAA (44%) were detected (Figure 3.19 e-g). About 2.7 times higher cRFA were generated in E stage effluent as compared to D_1 stage. The highest quantity of cRFA was generated in E stage effluent followed by D_1 and D_2 stages (Table 3.10). Out of the total cRFA generated the highest proportion came from CDAA (56%) followed by DCDAA (34%) and TCSA (10%) (Figure 3.19 h). By DED sequence 40, 43, and 72% reduction in generation of CDAA, DCDAA, and TCSA, respectively, was achieved in pulp bleaching effluents as compared to D/CED sequence. A total of 47% reduction in the generation of cRFA was observed as compared to D/CED sequence.

(c) cRFA generation during DE_PD sequence

For D_1 stage of DE_PD sequence the highest contribution came from CDAA (66%) followed by DCDAA (22%) and TCSA (12%). In E_P stage effluent only CDAA (65%) and DCDAA (35%) were detected. For D_2 stage also CDAA (53%) and DCDAA (47%) were the major contributors (Figure 3.20 a-c). About 2.5 times higher cRFA were generated in E_P stage effluent as compared to D_1 stage. The highest quantity of cRFA was generated in E_P stage effluent followed by D_1 and D_2 stages (Table 3.10). Out of the total cRFA generated the highest proportion came from CDAA (65%) followed by DCDAA (32%) and TCSA (3%) (Figure 3.20 d). By DE_PD sequence 51, 62, and 93% reduction in generation of CDAA, DCDAA, and TCSA, respectively, was achieved in pulp bleaching effluents as compared to D/CED sequence. A total of 62% reduction in the generation of cRFA was observed as compared to D/CED sequence.

(d) cRFA generation during ODED sequence

For D_1 and E stages of ODED sequence only CDAA, 73 and 69%, and DCDAA, 27 and 31%, respectively, were detected. While, in D_2 stage effluent only CDAA was detected (Figure 3.20 e-g). About 2.3 times higher cRFA were generated in E stage effluent as compared to D_1 stage. The highest quantity of cRFA was generated in E stage effluent followed by D_1 and D_2 stages (Table 3.10). Out of the total cRFA generated, CDAA contributed up to 71% and DCDAA 29% (Figure 3.20 h). By ODED sequence 75 and 84% reduction in levels of CDAA and DCDAA, respectively, was achieved in pulp bleaching effluents as compared to D/CED sequence. A total of 82.4% reduction in the generation of cRFA was observed as compared to D/CED sequence.

The generation of cRFA was highly reduced by ECF bleaching sequences using 100% ClO_2 as compared to D/CED sequence. The application of O_2 delignification and H_2O_2 reinforced extraction stage further reduced generation of cRFA significantly. These findings were found in good agreement with the literature [28, 29, 42]. The generation of highly substituted cRFA i.e. DCPAA and TCSA was highly reduced in ECF sequences. The generation of chlorinated cRFA is reduced during bleaching with ClO_2 due to elimination of ethylenic groups. Reaction with ethylenic groups generates epoxide structures which are ruptured by further reaction to form carbonyl group containing fragments [1].

3.3.5 BLEACHING ECONOMIC ANALYSIS

The economic analysis of any process change can be carried out either by measuring the operating costs (additional input costs) or value addition (gain in output costs). However, the assignment of economic value becomes difficult in case of intangible benefits associated with the variables. In such cases, the economic viability of a process can be assessed in terms of improved environmental performance and compliance with set regulatory standards. The process may suffer closure in case of non-compliance. In such circumstances, the increased input costs for making a process operational can be considered as investment cost and cost of closure for non-compliance as economic gain of investment. For the pulp bleaching economic analysis the costs associated with the following factors have been considered as input [60]:

1. The bleach chemical (O_2, $MgSO_4.7H_2O$, Cl_2, ClO_2, NaOH, and H_2O_2) costs for DED, DE_PD, and ODED sequences as compared to D/CED sequence.

2. The AOX abatement costs at source (by pulp bleaching technology modification) and by end-of-pipe effluent treatment using adsorption and ion exchange technologies (Rs 200/kg of AOX removed) [61] as per present price index have been considered as additional operation costs for meeting the set standards.
3. The intangible benefits associated with sustainable operations owing to environmental compliance through modified pulp bleaching sequences (O_2 pretreatment, replacement of Cl_2 by ClO_2, and H_2O_2 reinforced alkaline extraction), which would otherwise have been closed for non-compliance, are not considered for the present cost estimates.
4. The cost savings due to alkali recovery (about 90% NaOH is recovered) by oxygen stage effluent recycling to the recovery section have not been considered, which will further reduce the cost of ODED sequence.
5. CPCB, India has proposed standard of AOX at 1 kg/t of product manufactured with effect from 1st March, 2008 [62].

Table 3.2 depicts the chemical charge required for different pulp bleaching sequences for achieving 87% ISO target brightness. The cost of different pulp bleaching chemicals in India (2012) is mentioned in Table 3.12. These were obtained from nearby paper mills and chemical suppliers. Table 3.13 shows the chemical cost analysis for different pulp bleaching sequences for achieving 87% ISO target brightness. The results indicate that the total bleaching cost is higher for DED sequence followed by DE_PD, ODED, and D/CED sequences. If AOX abatement at the source (by pulp bleaching technology modification) is considered for meeting out discharge standards, then the additional costs needed are Rs 452/-, 362/-, and 309/- for using DED, DE_PD, and ODED sequences, respectively, as compared to D/CED sequence. If the additional costs required for AOX abatement at the source and for end-of-pipe effluent treatment of AOX (amount that has been reduced at source as compared to D/CED sequence) using adsorption and ion exchange technologies (Rs. 200/kg AOX removed) [61] are considered, then ODED sequence gave the highest cost savings (Rs 143/-) followed by DE_PD (Rs 48/-) sequence as compared to D/CED sequence. While, DED sequence was found to be having Rs 139/- higher cost as compared to D/CED sequence.

The lowest amount of AOX was generated for ODED sequence followed by DE_PD, DED, and D/CED sequences. D/CED sequence with high AOX generation can not be adopted in sight of AOX discharge standards. All other ECF bleaching sequences (DED, DE_PD, and ODED) were effective in reducing AOX generation below the set regulatory standard (1 kg/t of product). O_2 stage effluent can also be sent to the chemical recovery section which will further reduce the cost of ODED sequence. One of the main reasons for not adopting O_2 delignification process (particularly in small mills) is the high capital costs of O_2 delignification plant. But in order to meet AOX discharge standards and closing of the bleach cycle, the mills may look at O_2 as a pre-bleaching stage. The mills which will not be able to install O_2 pre-bleaching stage can meet up effluent discharge standards, particularly with regard to AOX, by using DE_PD sequence with 79% lesser AOX generation and Rs 48/- of cost savings as compared to D/CED sequence. While, DED sequence with 74% lesser AOX generation is costlier as compared to D/CED sequence. The economic analysis shows that ODED and DE_PD sequences can be adopted with regard to meeting AOX discharge standards and bleaching cost. The control of AOX in the effluent is one of the major environmental challenges before the pulp and paper industry. Hence, adoption of new cleaner bleaching technologies is the need of the hour.

Table 3.1 Oxygen delignification conditions

Parameter	Untreated	Sample 1	Sample 2	Sample 3
O_2 pressure (kg/cm^2)	----	6	6	6
Consistency (%)	----	10	10	10
Retention time (min)	----	75	75	75
Temperature (°C)	----	100	100	100
$MgSO_4.7H_2O$ (Kg/t O.D. pulp)	----	2	2	2
NaOH charge (kg/t O.D. pulp)	----	10	20	30
Kappa no.	15	9.1	8.3	7.4
Viscosity (cP)	13.9	12.8	12.2	11.3
Brightness (% ISO)	34.5	42.4	49.3	57.9

Table 3.2 Chemical charge (kg/t O.D. pulp) required for different bleaching sequences for achieving 87% ISO target brightness

Stage	Chemical	Chemical charge (kg/t O.D. pulp)			
		$D_{50}/C_{50}ED$	DED	DE_PD	ODED
O	O_2	------	------	------	20*
	NaOH	------	------	------	20
	$MgSO_4.7H_2O$	------	------	------	2
D/C or D_1	Cl_2	15.75	------	------	------
	ClO_2	5.99	13.97	11.98	6.63
E	NaOH	10	7	7	7
	H_2O_2	------	------	3	------
D_2	ClO_2	5.13	5.99	5.13	2.84
Final brightness (% ISO)		86.9	87.1	87.3	86.9

*[1]

Table 3.3 Generation (kg/t O.D. pulp) of BOD, COD, color, and AOX during different stages of D/CED, DED, DE$_P$D, and ODED sequences

Sequence	Stage	Quantity (kg/t O.D. pulp)			
		BOD	COD	Color	AOX
D/CED	D/C	3.0	14.1	13.4	2.20
	E	2.2	11.7	28.3	0.30
	D	1.1	1.8	0.6	0.10
DED	D_1	3.8	15.8	15.6	0.32
	E	3.1	12.8	18.4	0.28
	D_2	0.9	3.0	1.3	0.07
DE$_P$D	D_1	3.2	12.2	14.1	0.27
	E_P	2.5	10.1	16.7	0.23
	D_2	0.8	2.3	1.1	0.05
ODED	D_1	1.8	6.5	1.8	0.16
	E	1.5	5.1	2.0	0.14
	D_2	0.8	1.6	0.9	0.04

Table 3.6 Chlorophenolics generation (mg/t O.D. pulp) during different stages of DED sequence

S. No.	Compound	Quantity (mg/t O.D. pulp)			
		D_1	E	D_2	Total
1.	3-CP	9.0	85.0	0.6	94.6
2.	4-CP	3.6	25.6	0.6	29.8
3.	2,6-DCP	2.2	0.2	0.5	2.9
4.	2,5-DCP	5.0	2.9	0.3	8.2
5.	2,4-DCP	1.6	0.7	0.8	3.1
6.	2,3-DCP	0.5	0.3	0.5	1.3
7.	3,4-DCP	ND	1.3	1.2	2.5
8.	4-CG	43.5	201.2	9.6	254.3
9.	2,4,5-TCP	2.8	2.3	2.1	7.2
10.	2,3,6-TCP	2.2	ND	ND	2.2
11.	2,3,5-TCP	5.0	ND	ND	5.0
12.	2,4,6-TCP	0.5	0.4	ND	0.9
13.	4,5-DCG	186.7	203.9	12.7	403.3
14.	2,3,4-TCP	2.5	2.0	0.9	5.4
15.	4,6-DCG	2.7	2.2	0.8	5.7
16.	3,6-DCC	74.0	55.0	18.0	147.0
17.	3,5-DCC	23.2	21.6	1.6	46.4
18.	3,4,6-TCG	1.7	2.1	ND	3.8
19.	3,4,5-TCG	0.4	0.8	ND	1.2
20.	4,5,6-TCG	0.9	3.6	ND	4.5
21.	5,6-DCV	2.0	1.9	ND	3.9
22.	PCP	2.3	2.2	ND	4.5
23.	Tet-CG	2.5	2.6	ND	5.1
24.	TCS	1.9	ND	ND	1.9
25.	Tet-CC	9.1	7.1	ND	16.2
26.	2,6-DCSA	11.7	31.1	ND	42.8
Total		**397.5**	**656.0**	**50.2**	**1103.7**

ND - not detected.

Table 3.7 Chlorophenolics generation (mg/t O.D. pulp) during different stages of DE_PD sequence

S. No.	**Compound**	**Quantity (mg/t O.D. pulp)**			
		D_1	**E_P**	**D_2**	**Total**
1.	3-CP	3.3	40.4	0.9	44.6
2.	4-CP	1.2	0.4	0.1	1.7
3.	2,6-DCP	1.3	ND	ND	1.3
4.	2,5-DCP	4.0	18.4	1.0	23.4
5.	2,4-DCP	0.4	0.6	0.1	1.1
6.	2,3-DCP	ND	ND	ND	ND
7.	3,4-DCP	1.2	1.1	1.0	3.3
8.	4-CG	46.8	131.5	ND	178.3
9.	2,4,5-TCP	2.7	2.1	1.6	6.4
10.	2,3,6-TCP	ND	ND	ND	ND
11.	2,3,5-TCP	ND	ND	ND	ND
12.	2,4,6-TCP	ND	ND	ND	ND
13.	4,5-DCG	123.7	180.1	14.1	317.9
14.	2,3,4-TCP	1.7	1.7	0.7	4.1
15.	4,6-DCG	0.8	1.8	ND	2.6
16.	3,6-DCC	64.3	ND	ND	64.3
17.	3,5-DCC	18.6	ND	ND	18.6
18.	3,4,6-TCG	ND	ND	ND	ND
19.	3,4,5-TCG	0.3	ND	ND	0.3
20.	4,5,6-TCG	ND	1.5	ND	1.5
21.	5,6-DCV	ND	1.8	ND	1.8
22.	PCP	ND	ND	ND	ND
23.	Tet-CG	ND	ND	ND	ND
24.	TCS	ND	ND	ND	ND
25.	Tet-CC	7.4	5.3	0.9	13.6
26.	2,6-DCSA	ND	6.5	0.5	7.0
Total		**277.7**	**393.2**	**20.9**	**691.8**

ND - not detected.

Table 3.8 Chlorophenolics generation (mg/t O.D. pulp) during different stages of ODED sequence

S. No.	Compound	Quantity (mg/t O.D. pulp)			
		D_1	E	D_2	Total
1.	3-CP	2.4	1.8	1.8	6.0
2.	4-CP	0.6	0.4	0.3	1.3
3.	2,6-DCP	0.7	0.9	0.1	1.7
4.	2,5-DCP	2.4	3.5	0.7	6.6
5.	2,4-DCP	0.2	0.7	0.1	1.0
6.	2,3-DCP	ND	0.5	ND	0.5
7.	3,4-DCP	1.9	2	ND	3.9
8.	4-CG	5.9	46.6	3.5	56.0
9.	2,4,5-TCP	16.9	17	0.7	34.6
10.	2,3,6-TCP	ND	1.2	ND	1.2
11.	2,3,5-TCP	ND	2.8	ND	2.8
12.	2,4,6-TCP	0.4	ND	ND	0.4
13.	4,5-DCG	13.2	167.1	2.7	183.0
14.	2,3,4-TCP	1.1	2.1	1.1	4.3
15.	4,6-DCG	0.8	1.4	1.1	3.3
16.	3,6-DCC	59.5	ND	ND	59.5
17.	3,5-DCC	30.9	ND	ND	30.9
18.	3,4,6-TCG	2	ND	ND	2.0
19.	3,4,5-TCG	0.5	ND	0.8	1.3
20.	4,5,6-TCG	ND	ND	0.3	0.3
21.	5,6-DCV	4.4	5	ND	9.4
22.	PCP	ND	ND	ND	ND
23.	Tet-CG	ND	ND	ND	ND
24.	TCS	ND	2.8	ND	2.8
25.	Tet-CC	6.6	4	ND	10.6
26.	2,6-DCSA	3.9	4.1	ND	8.0
Total		**154.3**	**263.9**	**13.2**	**431.4**

ND - not detected.

Table 3.9 RT (min), RF (pg), and EE (%) of various cRFA reference compounds (methyl derivatives) separated on OPTIMA - 1 - MS column

S. No.	Compound	RT (min)	RF (pg)	EE (%)
1.	9,10-Dichlorostearic acid (DCSA)*	29.74	0.10	93
2.	Chlorodehydroabietic acid (CDAA)$^\#$	30.24	0.17	93
3.	12,14-Dichlorodehydroabietic acid (DCDAA)$^\#$	37.56	0.42	97
4.	9,10,12,13-Tetrachlorostearic acid (TCSA)*	41.31	0.25	104

* chloro-fatty acids (cFA); # chloro-resin acids (cRA)

Table 3.10 Generation of cRFA (g/t O.D. pulp) during different stages of D/CED, DED, DE$_P$D, and ODED sequences

Bleaching stage	Quantity (g/t O.D. pulp)			
	CDAA	DCDAA	TCSA	Total
D/CED Sequence				
D/C	1.43	0.85	0.24	2.52
E	3.74	2.43	1.74	7.91
D	0.20	0.14	ND	0.34
Total	5.37	3.42	1.98	10.77
DED Sequence				
D_1	0.99	0.33	0.19	1.51
E	2.13	1.54	0.36	4.03
D_2	0.12	0.09	ND	0.21
Total	3.24	1.96	0.55	5.75
DE$_P$D Sequence				
D_1	0.75	0.25	0.14	1.14
E_P	1.80	0.98	ND	2.78
D_2	0.08	0.07	ND	0.15
Total	2.63	1.30	0.14	4.07
ODED Sequence				
D_1	0.41	0.15	ND	0.56
E	0.91	0.40	ND	1.31
D_2	0.03	ND	ND	0.03
Total	1.35	0.55	0	1.90

ND - not detected.

Table 3.11 Generation of cRA and cFA (g/t O.D. pulp) during different stages of D/CED, DED, DE_PD, and ODED sequences

Bleaching stage	Quantity (g/t O.D. pulp)		
	cRA	**cFA**	**Total**
D/CED Sequence			
D/C	2.28	0.24	2.52
E	6.17	1.74	7.91
D	0.34	ND	0.34
Total	8.79	1.98	10.77
DED Sequence			
D_1	1.32	0.19	1.51
E	3.67	0.36	4.03
D_2	0.21	ND	0.21
Total	5.20	0.55	5.75
DE_PD Sequence			
D_1	1.00	0.14	1.14
E_P	2.78	ND	2.78
D_2	0.15	ND	0.15
Total	3.93	0.14	4.07
ODED Sequence			
D_1	0.56	ND	0.56
E	1.31	ND	1.31
D_2	0.03	ND	0.03
Total	1.90	-------	1.90

ND – not detected

Table 3.12 Cost of chemicals (Rs/kg) used for pulp bleaching in India in 2012

Chemical	Cost (Rs/kg)
Chlorine (Cl_2)	12
Chlorine dioxide (ClO_2)	80
Sodium hydroxide (NaOH)	22
Hydrogen peroxide (H_2O_2)	46
Oxygen (O_2)	10
Magnesium sulphate ($MgSO_4$)	28

Table 3.13 Chemical cost (Rs/t O.D. pulp) analysis for different pulp bleaching sequences for attaining 87% ISO target brightness

Sequence	Bleaching cost (Rs/t O.D. pulp)		AOX (kg/t O.D. pulp)		AOX abatement cost (Rs/kg)		
	Pre-treatment	Bleach chemical	Generation	Reduction at source	At source	EPT*	Savings
D/CED	------	1299	2.60	------	------	------	------
DED	------	1751	0.67	1.93	+452	386	-139
DE_pD	------	1661	0.55	2.05	+362	410	+48
ODED	696	1608#	0.34	2.26	+309	452	+143

* End of pipe treatment cost for AOX (which was reduced at source as compared to D/CED sequence) using adsorption and ion exchange methods (200 Rs/kg) [61]; # Including cost of O_2 pre-treatment

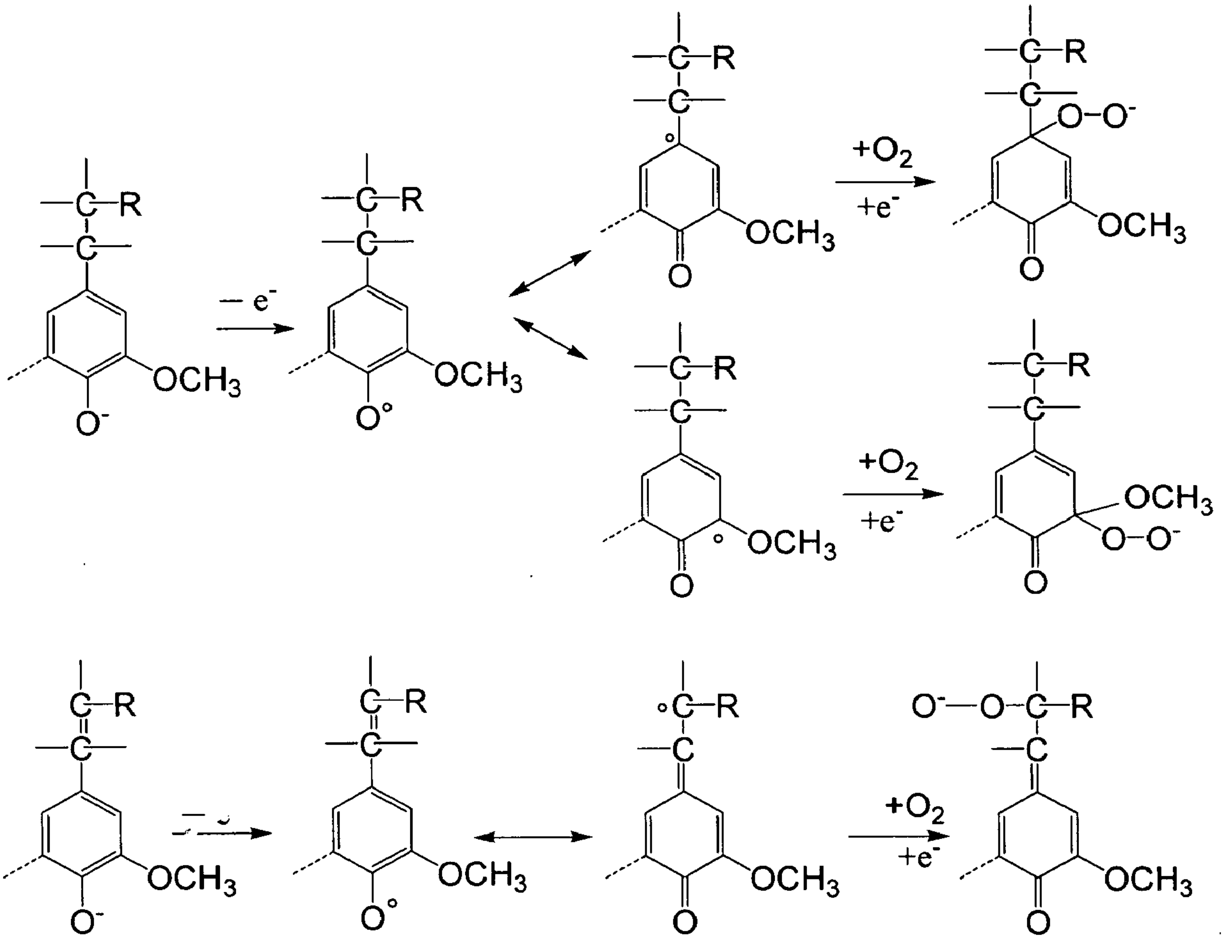


Figure 3.1 Initial reactions during oxygen delignification [1]

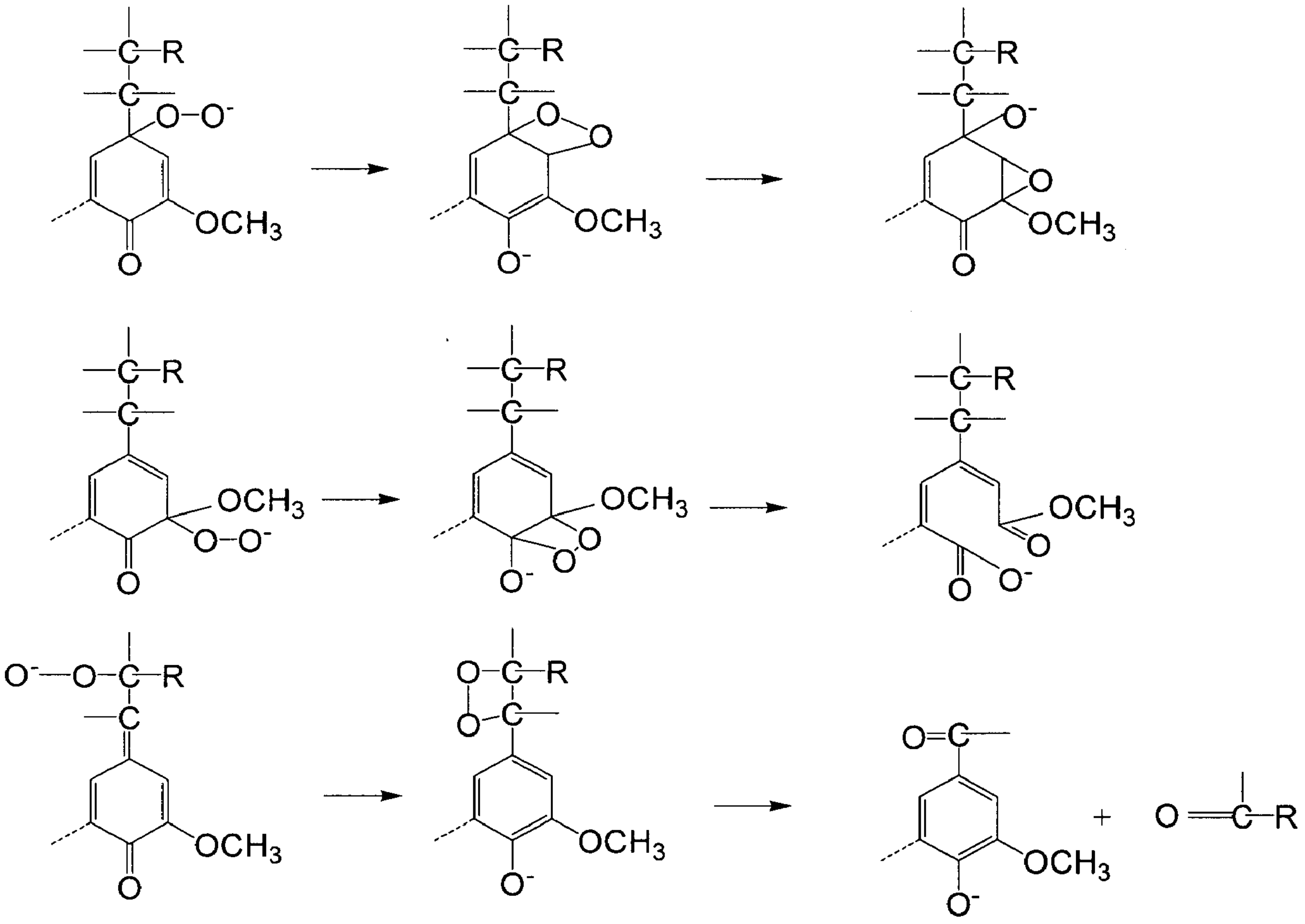
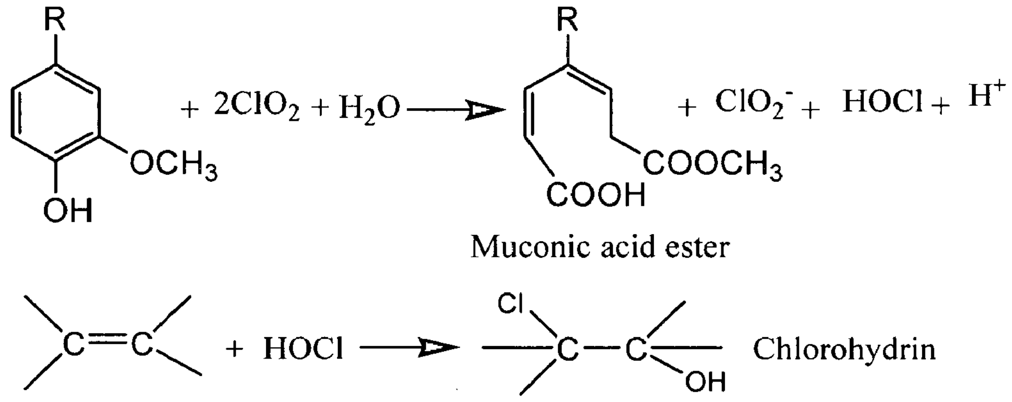


Figure 3.2 Reactions of intermediate hydroperoxides during oxygen delignification [1]

$HOROCH_3 + 2ClO_2 + H_2O \longrightarrow HOOROOCH_3 + ClO_2^- + HOCl + H^+$



$RH + HOCl \longrightarrow RCl + H_2O$

$HOCl + HCl \rightleftharpoons Cl_2 + H_2O$

Figure 3.3 Reactions of chlorine dioxide during pulp bleaching [21]

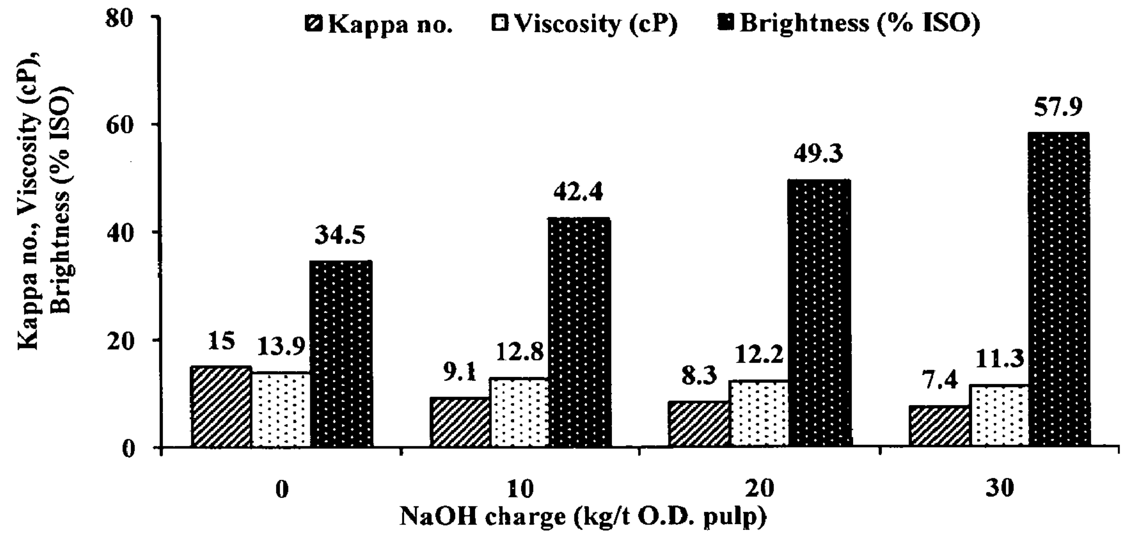
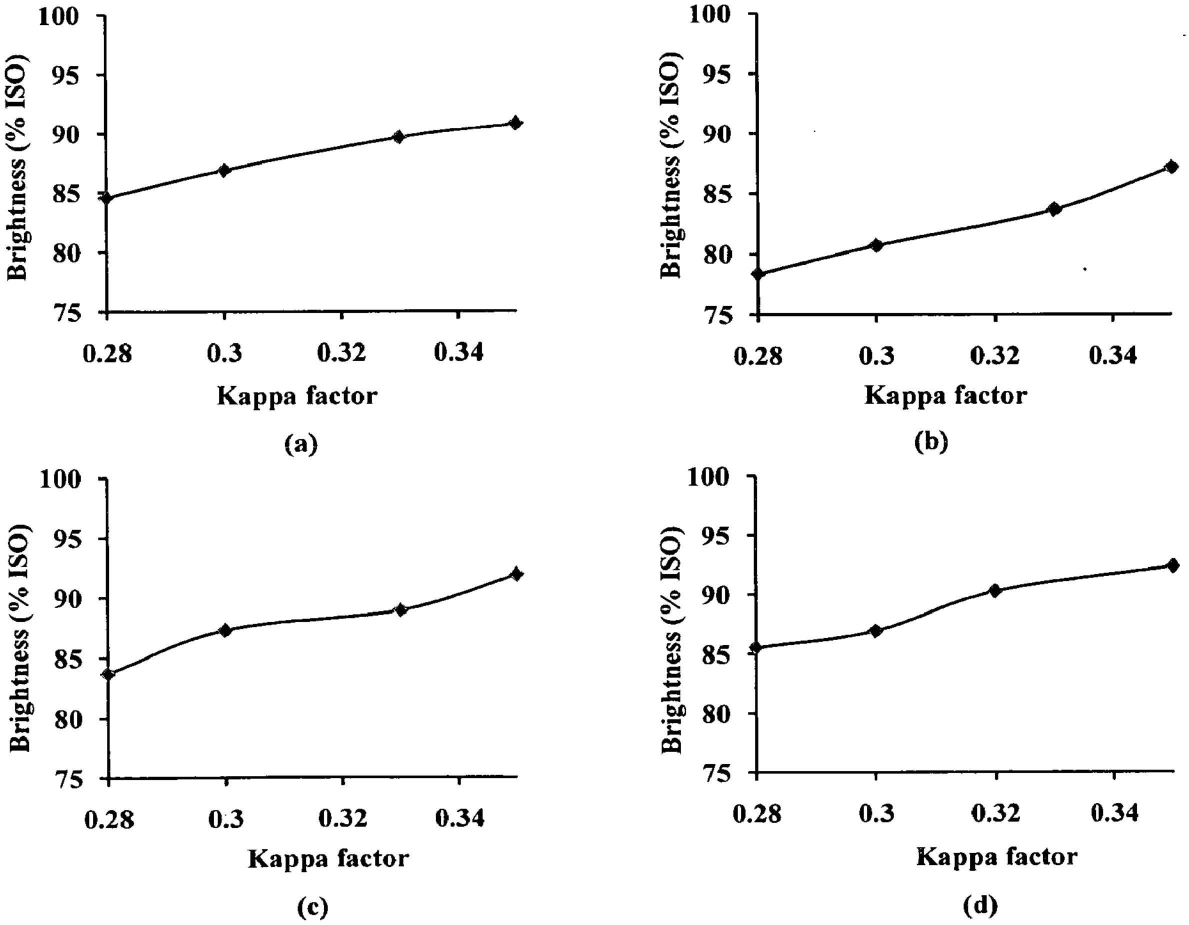


Figure 3.4 Effect of alkali charge during oxygen delignification on pulp kappa number, viscosity (cP), and brightness (% ISO)



(a)

(b)

(c)

(d)

Figure 3.5 Effect of kappa factor on pulp brightness during (a) D/CED, (b) DED, (c) DE$_P$D, and (d) ODED sequences for 87% ISO target brightness

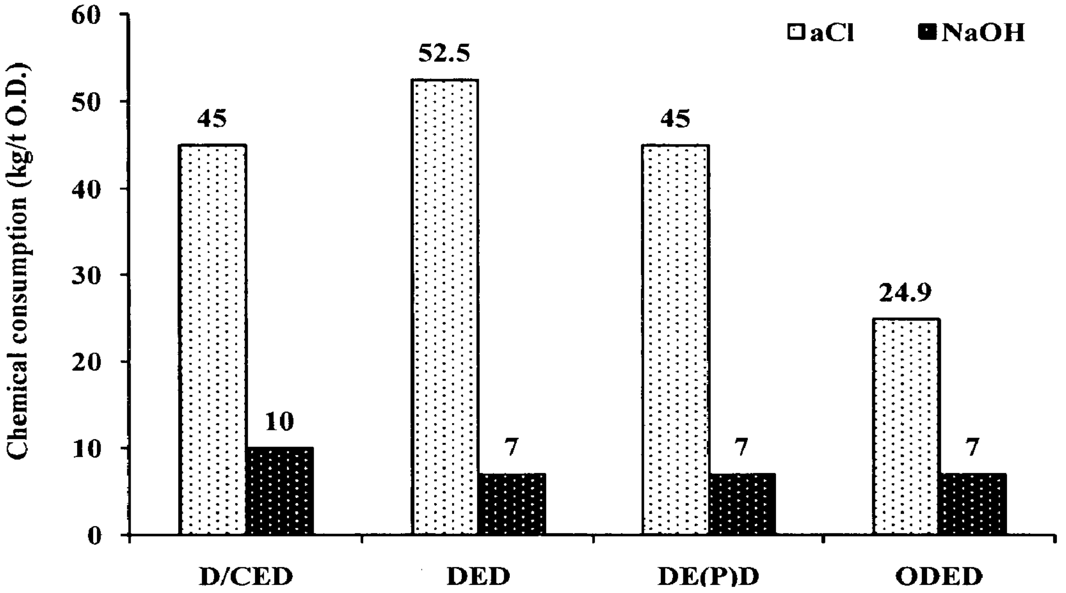


Figure 3.6 Chemical consumption during different pulp bleaching sequences

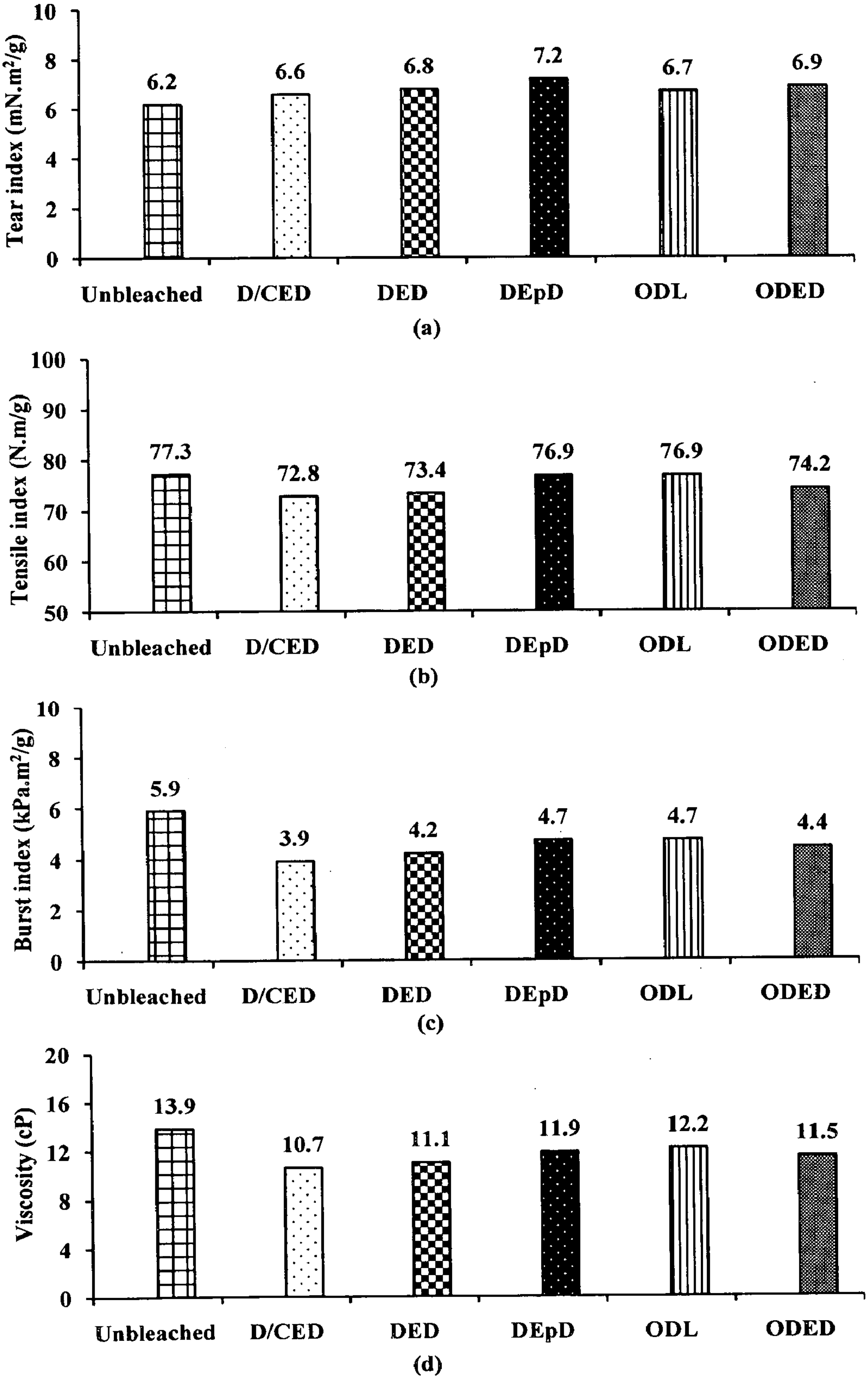


Figure 3.7 Effect of different bleaching sequences on pulp: (a) Tear index, (b) Tensile index, (c) Burst index, and (d) Viscosity

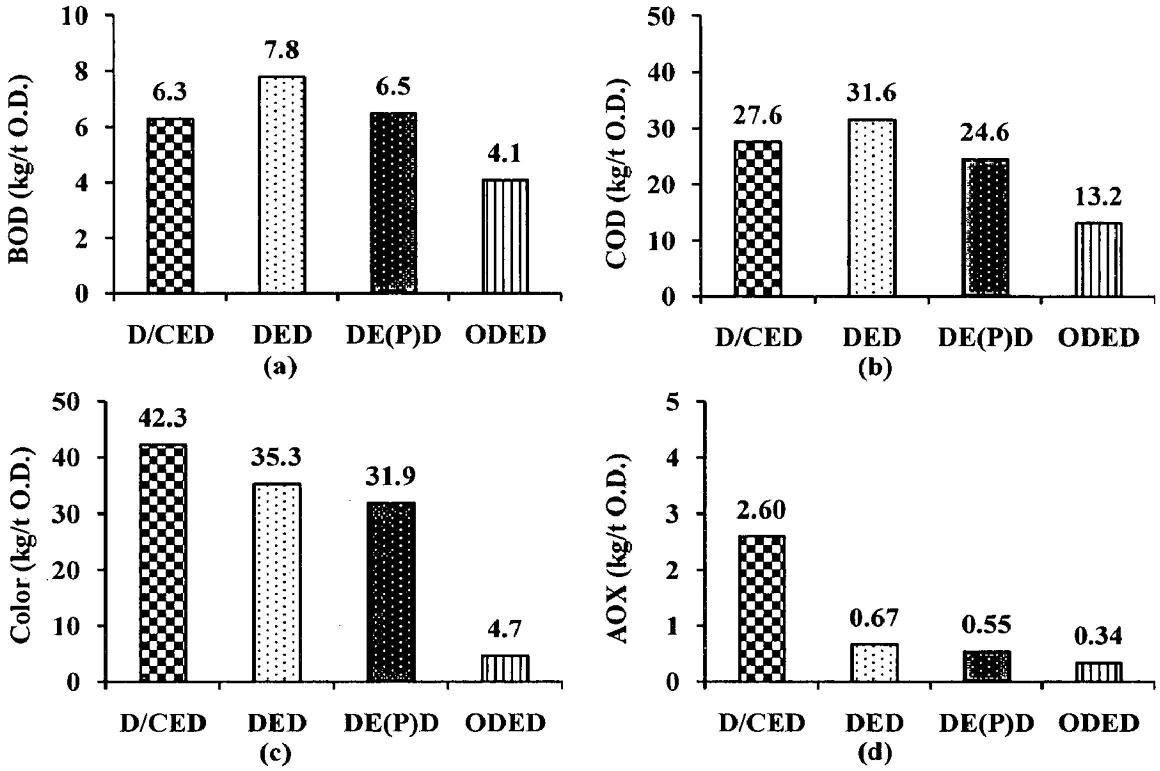


Figure 3.8 Generation (kg/t O.D. pulp) of (a) BOD, (b) COD, (c) Color, and (d) AOX during different bleaching sequences

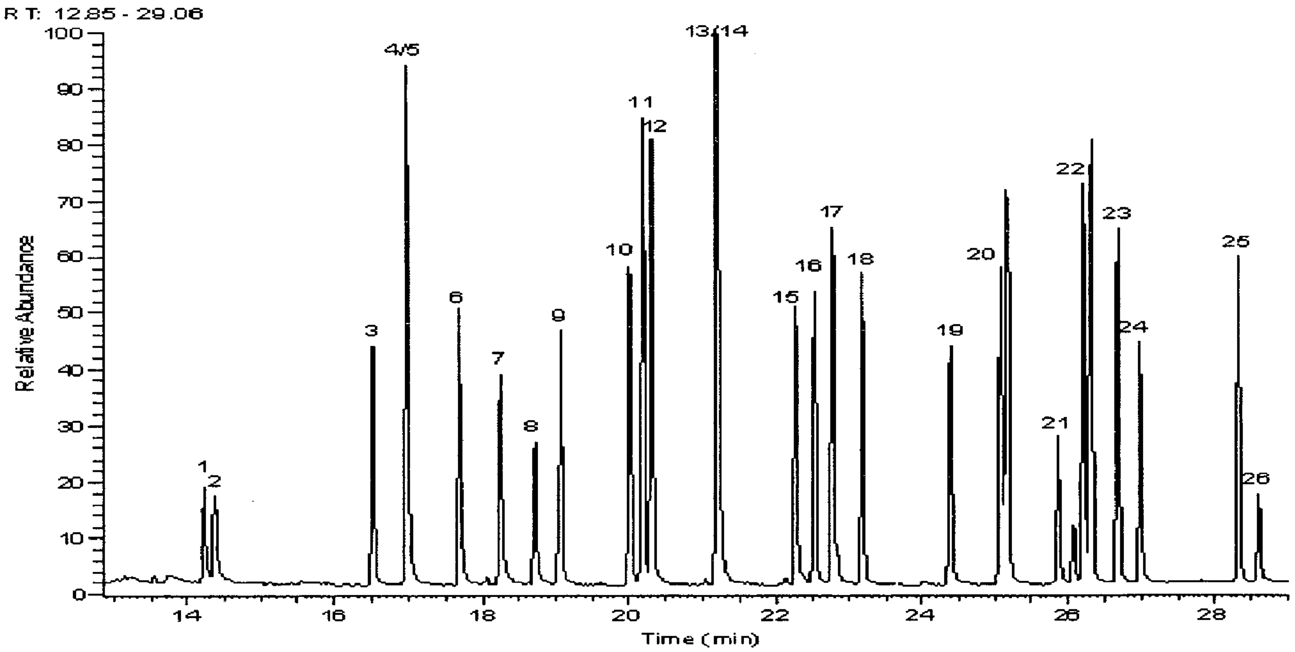
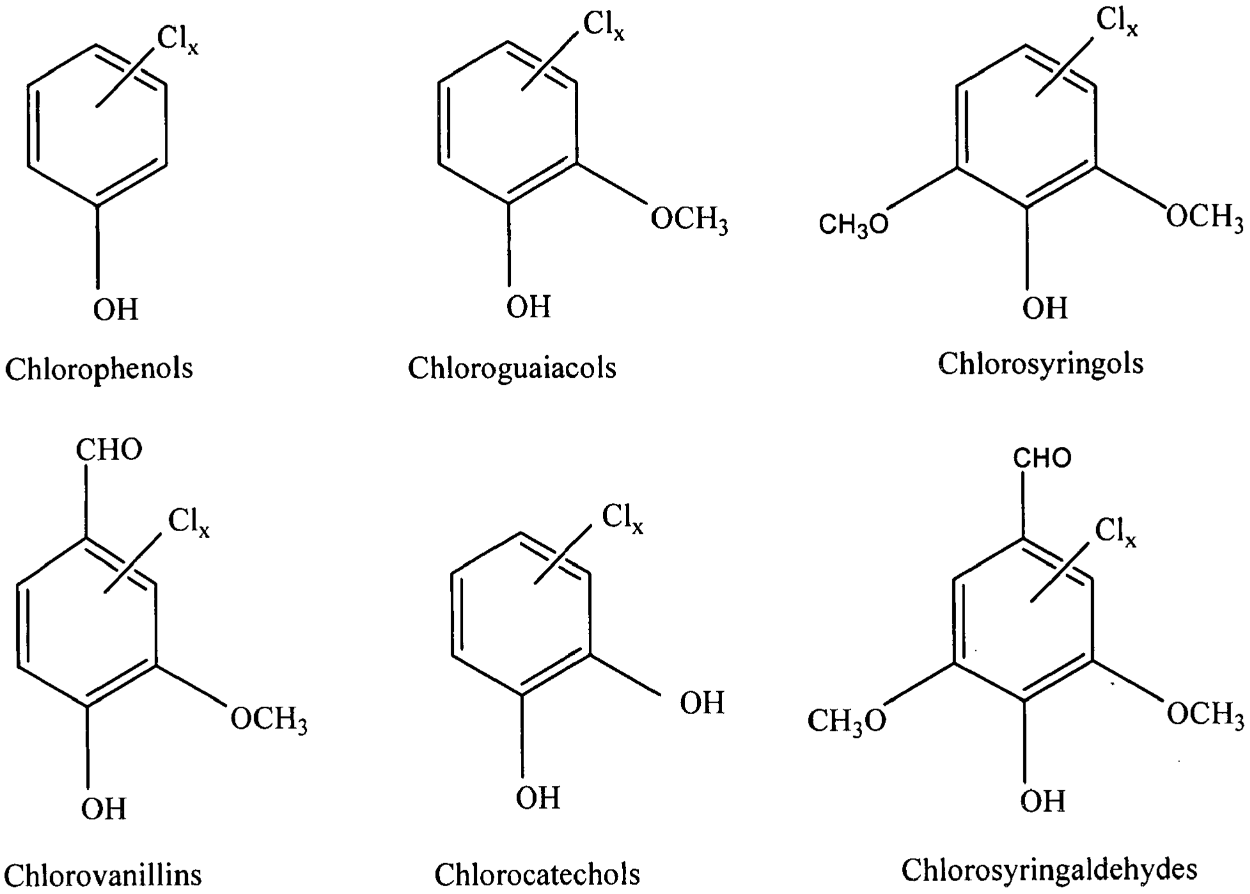


Figure 3.9 Chromatogram showing separation of a mixture of pure chlorophenolic compounds



Chlorophenols Chloroguaiacols Chlorosyringols

Chlorovanillins Chlorocatechols Chlorosyringaldehydes

Figure 3.10 Structure of various chlorophenolic compounds by chemical family

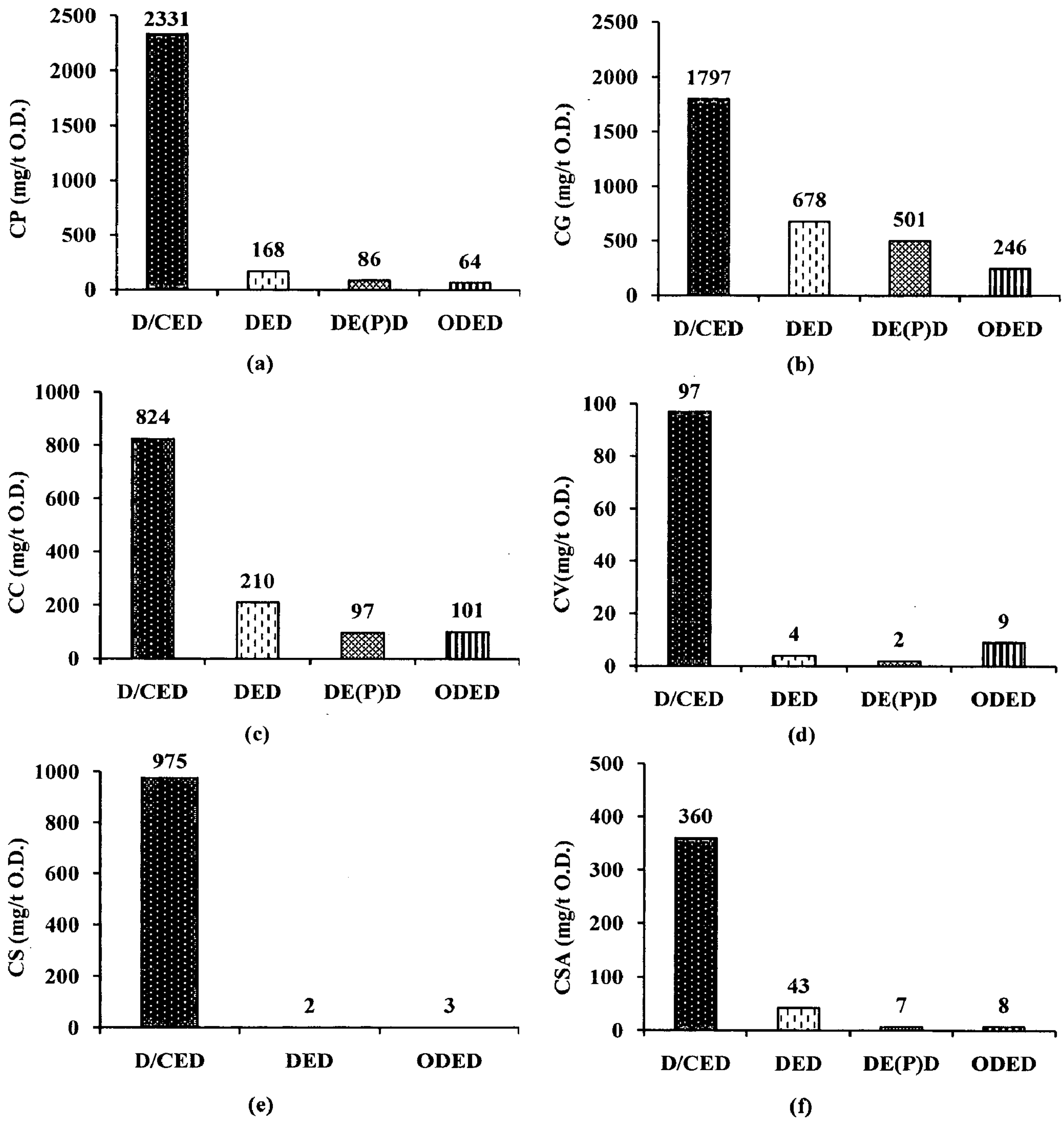


Figure 3.11 Generation of chlorophenolics (mg/t O.D. pulp) by chemical family during D/CED, DED, DE$_P$D, and ODED sequences

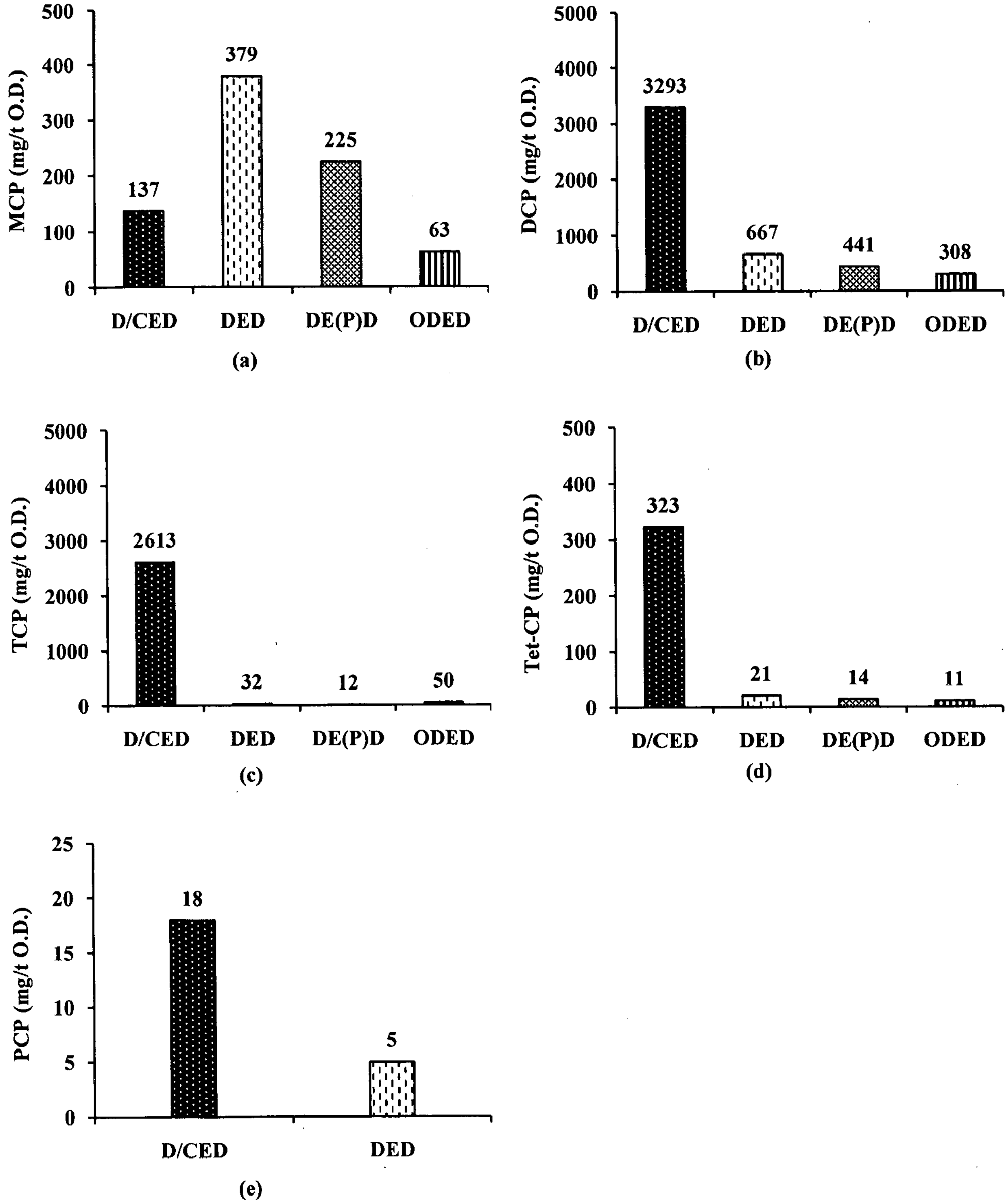


Figure 3.12 Generation of chlorophenolics (mg/t O.D. pulp) by number of attached Cl_2 atoms during D/CED, DED, DE_PD, and ODED sequences

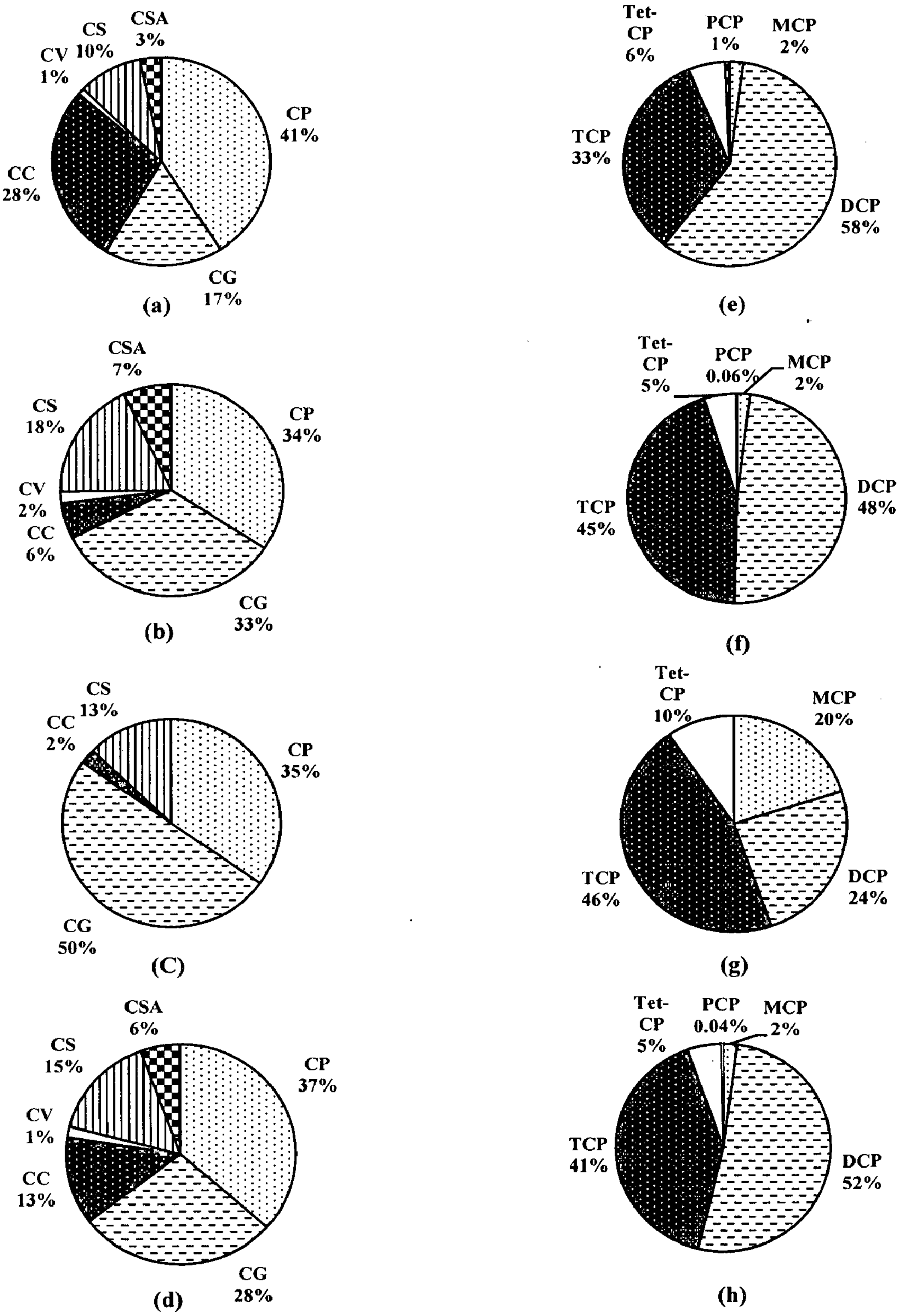


Figure 3.13 Generation of chlorophenolics (%) by chemical family (a-d) and number of attached Cl_2 atoms (e-h) in: D/C (a and e), E (b and f), and D (c and g) stage effluents of D/CED sequence and total quantity (d and h)

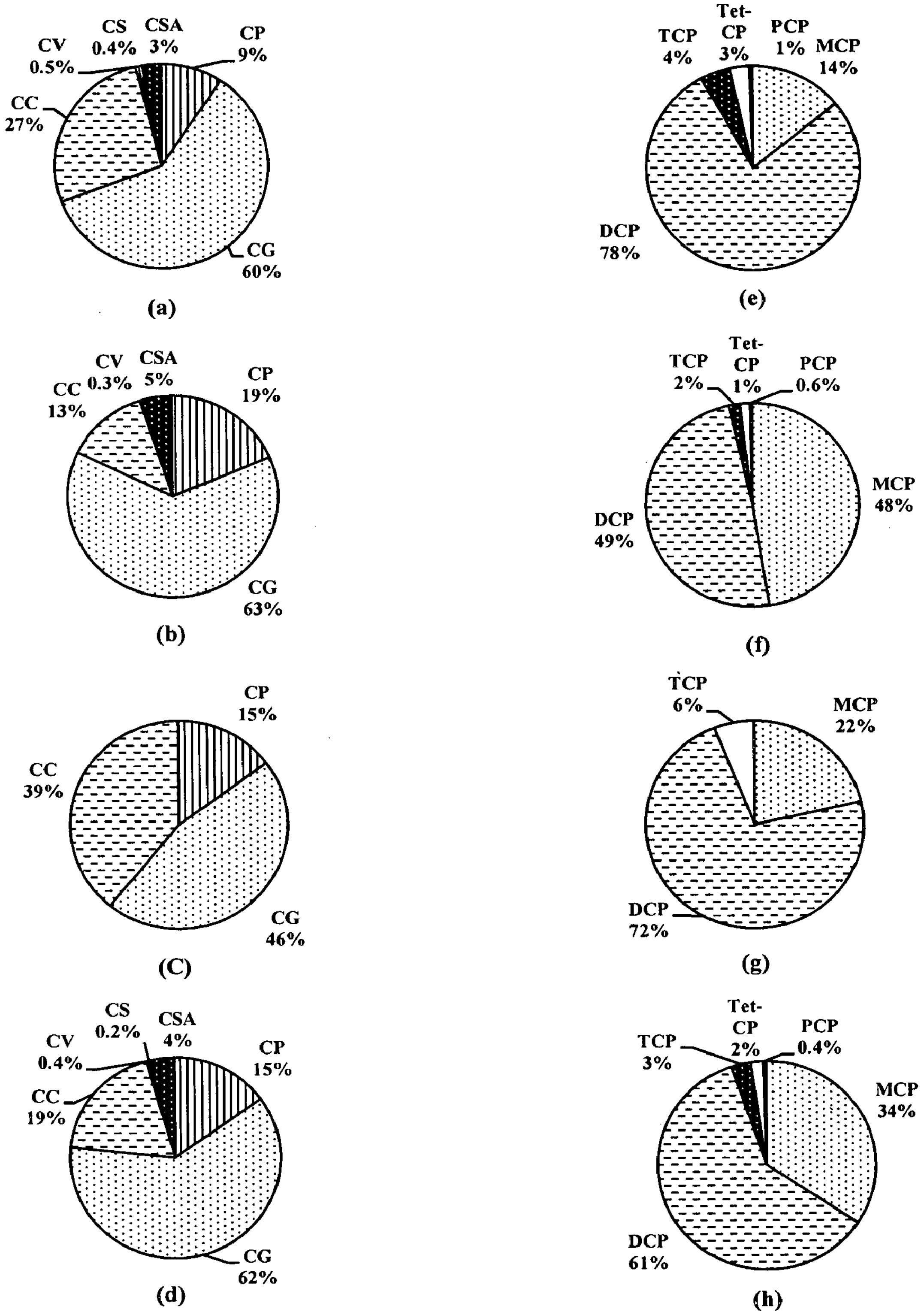
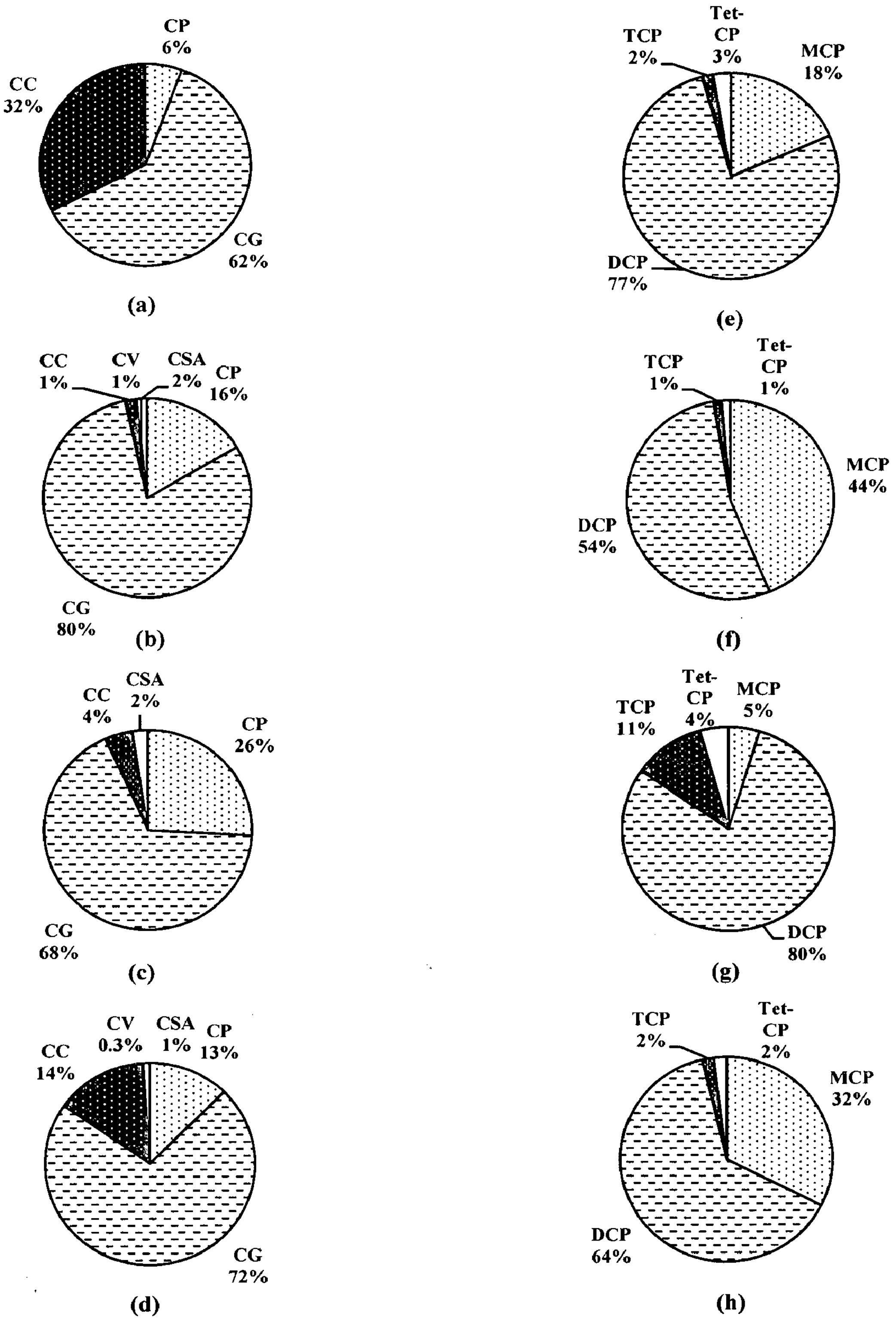


Figure 3.14 Generation of chlorophenolics (%) by chemical family (a-d) and number of attached Cl_2 atoms (e-h) in: D_1 (a and e), E (b and f), and D_2 (c and g) stage effluents of DED sequence and total quantity (d and h)



(a) (b) (c) (d) (e) (f) (g) (h)

Figure 3.15 Generation of chlorophenolics (%) by chemical family (a-d) and number of attached Cl_2 atoms (e-h) in: D_1 (a and e), E_P (b and f), and D_2 (c and g) stage effluents of DE_PD sequence and total quantity (d and h)

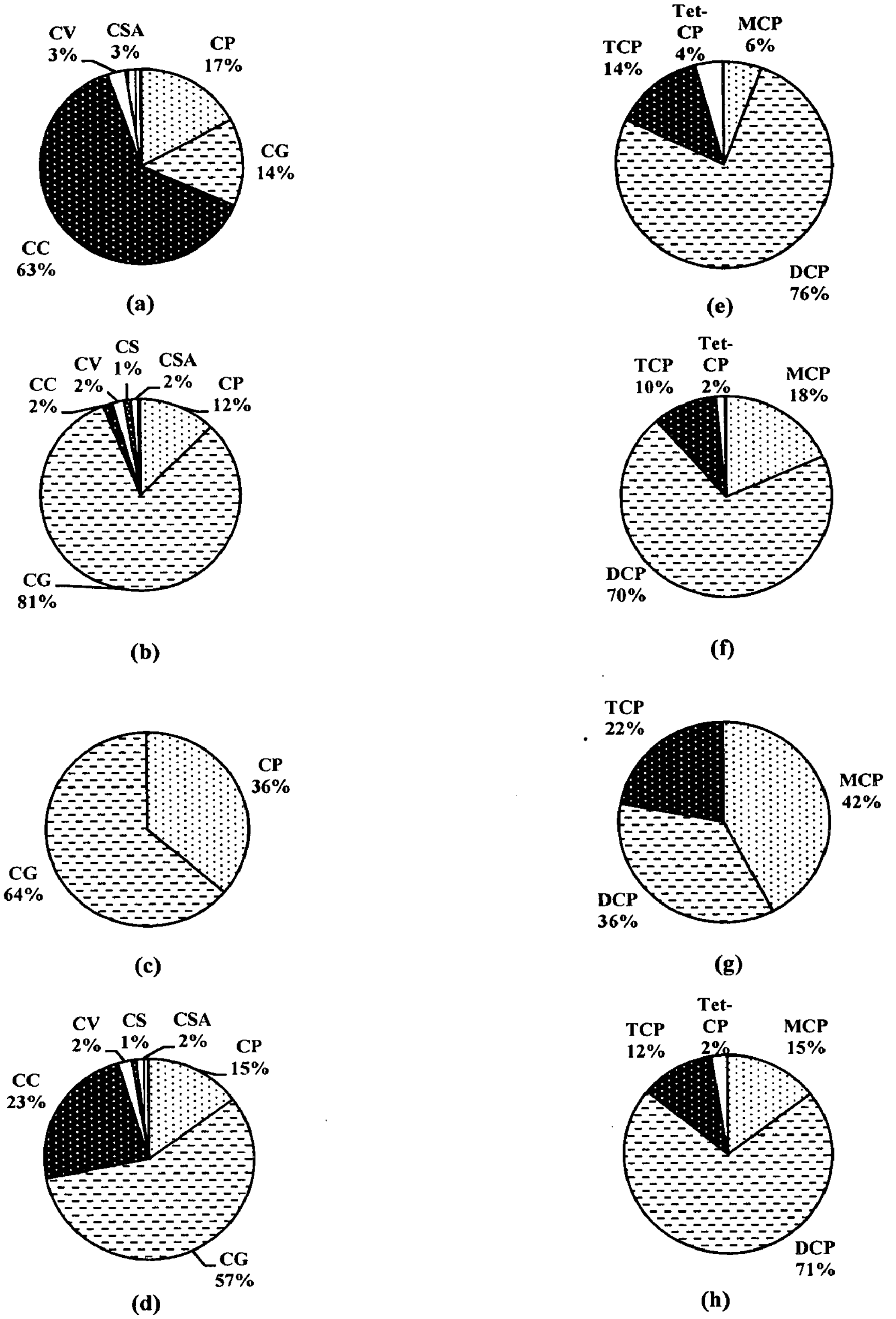


Figure 3.16 Generation of chlorophenolics (%) by chemical family (a-d) and number of attached Cl_2 atoms (e-h) in: D_1 (a and e), E (b and f), and D_2 (c and g) stage effluents of ODED sequence and total quantity (d and h)

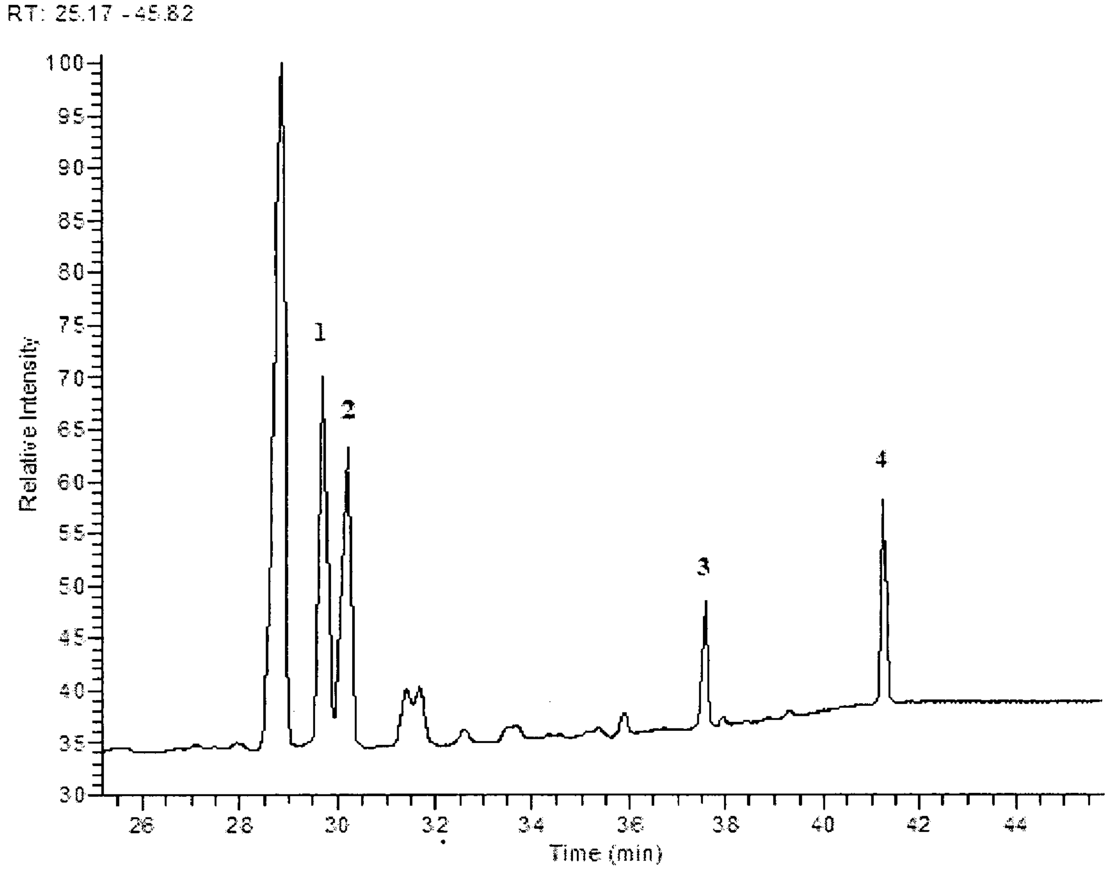
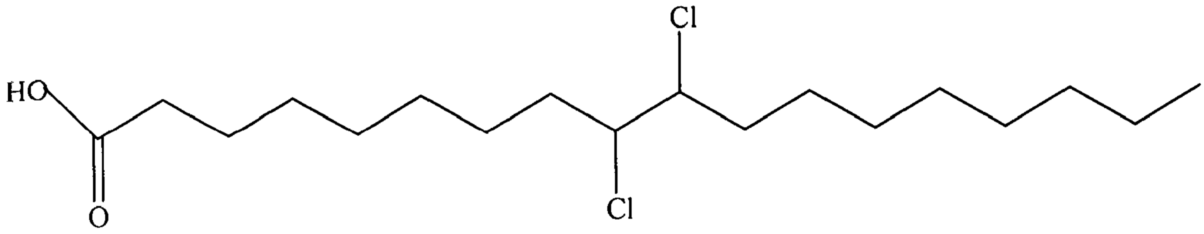
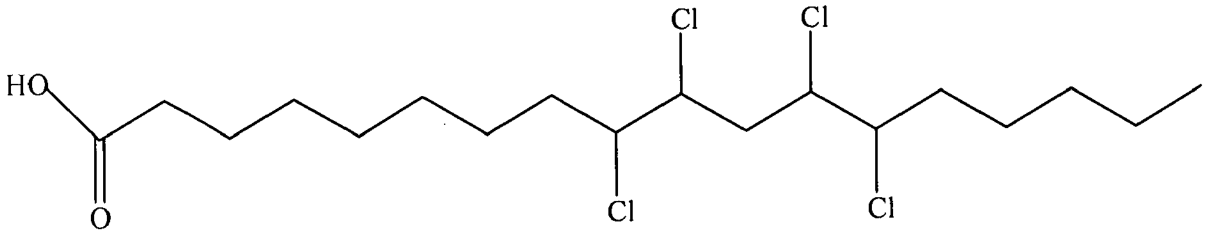


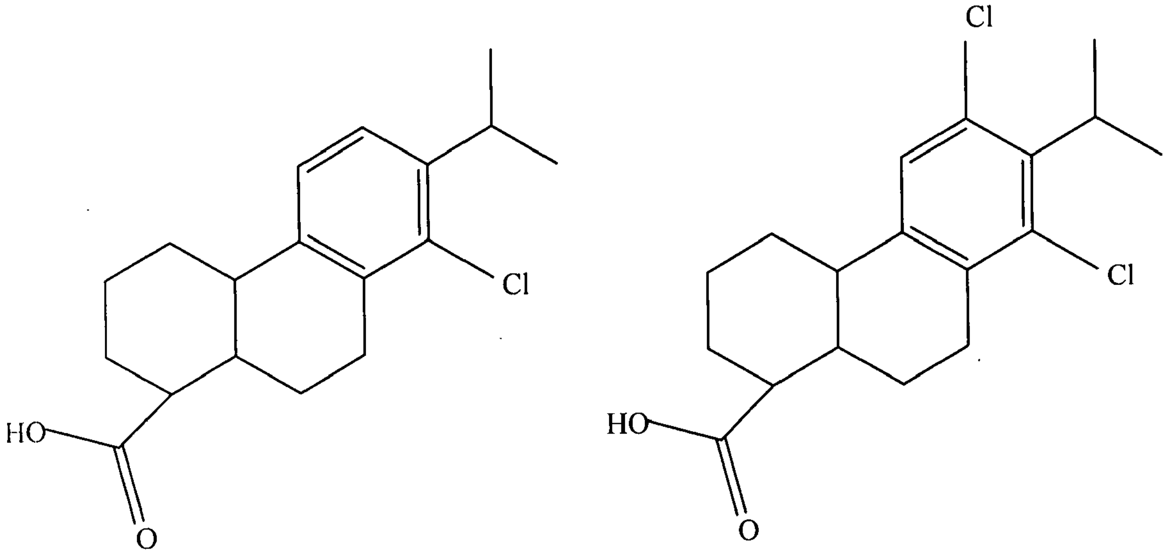
Figure 3.17 Chromatogram showing separation of a mixture of pure cRFA compounds



9,10-Dichlorostearic acid



9,10,12,13-Tetrachlorostearic acid



14-Chlorodehydroabietic acid

12,14-Dichlorodehydroabietic acid

Figure 3.18 Structure of various chloro-resin and fatty acids

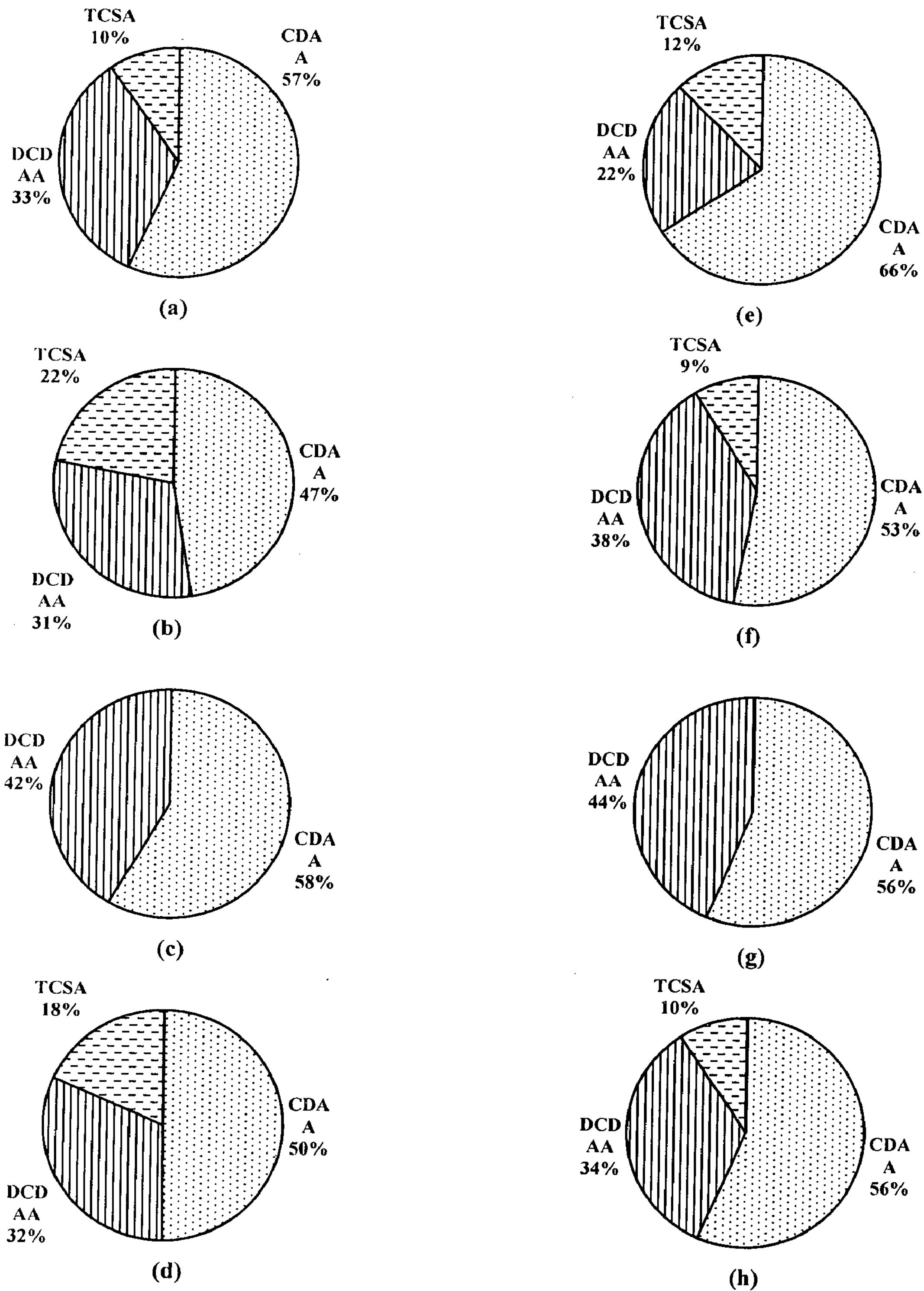


Figure 3.19 Generation of cRFA (%) in different stage effluents of D/CED: D/C (a), E (b), and D (c); DED: D_1 (e), E (f), and D_2 (g), sequences, and total quantity: D/CED (d) and DED (h)

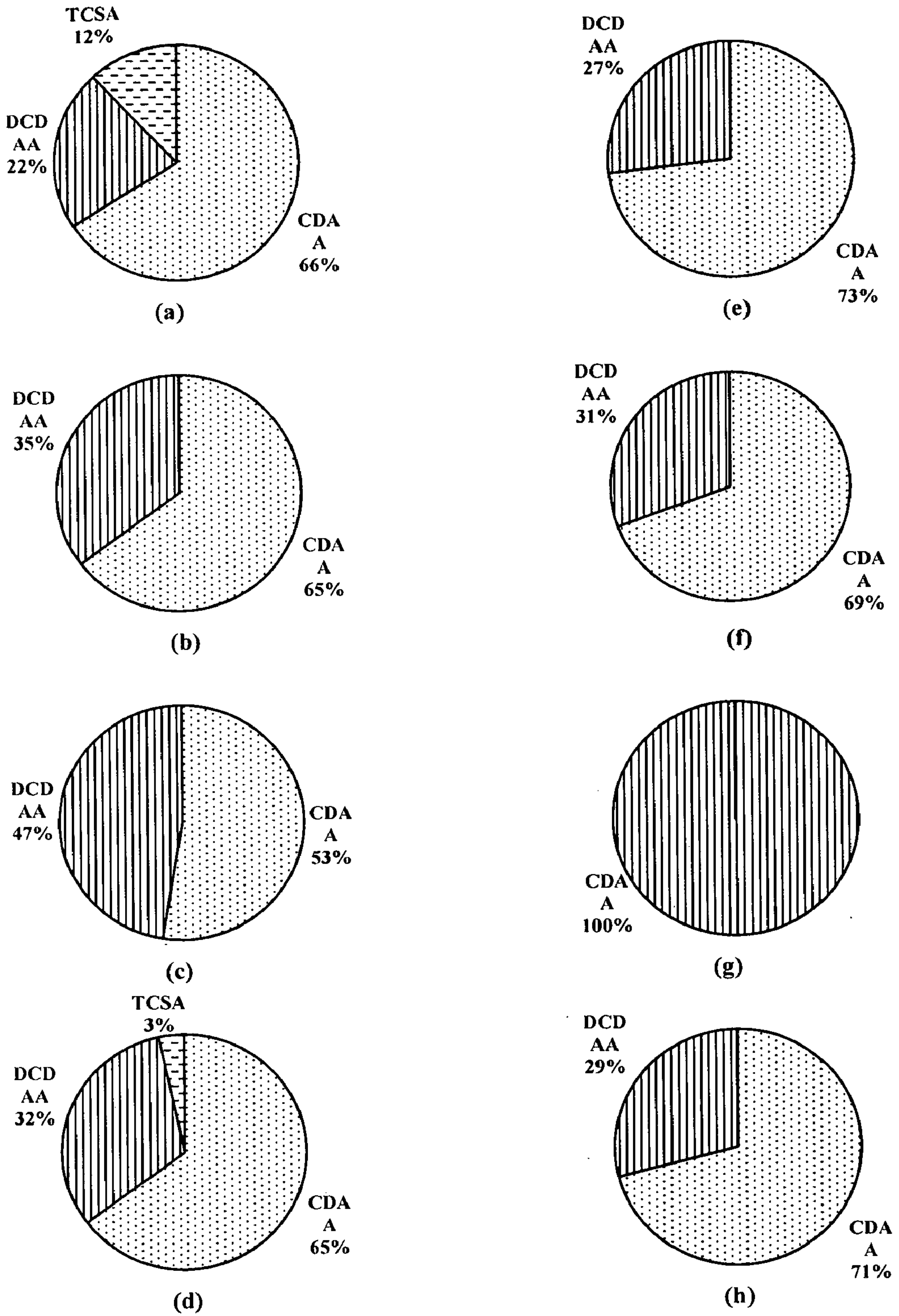


Figure 3.20 Generation of cRFA (%) in different stage effluents of DE$_P$D: D$_1$ (a), E$_P$ (b), and D$_2$ (c); ODED: D$_1$ (e), E (f), and D$_2$ (g), sequences, and total quantity: DE$_P$D (d) and ODED (h)

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CHAPTER 4
EFFLUENT TREATMENT STUDIES

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4.1 INTRODUCTION

The pulp produced by chemical pulping requires bleaching to produce bright pulp. These operations are known to generate various toxic and bio-refractory chlorinated organic compounds in the paper mill effluents [1-5]. These compounds are hazardous to the environment if discharged untreated. Conventional biological effluent treatment processes are not effective for the degradation of many of these organics and removal of color from paper mill effluents. Hence, treatment with some advanced oxidation processes (AOPs) is needed. AOPs rely on the hydroxyl radicals ($OH^{\bullet}$), which are generated in-situ, for the degradation of recalcitrant molecules into biodegradable compounds [6-8].

Photocatalysis, one of the AOPs, is an important alternative because it causes the complete mineralisation of a wide range of organics without any harmful environmental impact [9-14]. TiO_2 photocatalysis has been utilised effectively for the remediation of pollutants from pulp and paper mill effluents with promising results [5, 8, 15-17]. Perez et al. [18] reported that photocatalytic oxidation can efficiently reduce the organic load from elemental chlorine free (ECF) bleaching effluent. Balcioglu and Cecen [19] reported increase in the biodegradability of the bleaching effluent after photocatalysis. Perez et al. [20] reported that photocatalysis is efficient for the removal of adsorbable organic halides (AOX, 95%), total organic carbon (TOC, 50%), total phenols, and toxicity from the pulp bleaching effluent.

4.2 PRINCIPLE BEHIND TiO_2 PHOTOCHEMISTRY

When a photon of light ($\lambda < 390$ nm), having energy equal to or greater than the band gap energy (3.2 eV for anatase form of TiO_2), strikes the catalyst surface, an electron (e^-) is raised from valence band (vb) to the conduction band (cb) leaving behind a hole (h^+_{vb}) (Eq. 4.1) [16, 21]. The e^-_{cb}/h^+_{vb} pair can be trapped at or near TiO_2 surface and participate in e^- transfer reactions across the interface with the adsorbed pollutants (Figure 4.1) [22].

$$TiO_2 + hv \rightarrow e^-_{cb} + h^+_{vb} \tag{4.1}$$

The h^+_{vb} can either directly oxidize a wide range of adsorbed pollutants or produce $OH^•$ radicals (from adsorbed H_2O/OH^- ion) (Eq. 4.2 and 4.3) which can also oxidize pollutants non-selectively (Eq. 4.12 and 4.13). The e^-_{cb}/h^+_{vb} pair can also recombine at the surface and in the bulk phase, respectively, releasing the absorbed light energy as heat (Eq. 4.4). The e^-_{cb} is a strong reducing agent [7, 22] which is readily taken by adsorbed O_2 to produce superoxide radical ($O_2^{•-}$) (Eq. 4.5), thus preventing e^-_{cb}/h^+_{vb} recombination.

$$h^+_{vb} + H_2O_{ads} \rightarrow OH^•_{ads} + H^+ \qquad (4.2)$$

$$h^+_{vb} + OH^-_{ads} \rightarrow OH^•_{ads} \qquad (4.3)$$

$$e^-_{cb} + h^+_{vb} \rightarrow heat \qquad (4.4)$$

$$e^-_{cb} + O_{2ads} \rightarrow O^{•-}_{2ads} \qquad (4.5)$$

The $O_2^{•-}$ radical can further participate in contaminant degradation reactions through a series of redox reactions (Eq. 4.6-4.9) [7, 23, 24].

$$O_2^{•-} + H^+ \rightarrow HOO^• \qquad (4.6)$$

$$e^-_{cb} + HOO^• \rightarrow HO_2^- \qquad (4.7)$$

$$HOO^- + H^+ \rightarrow H_2O_2 \qquad (4.8)$$

$$H_2O_2 + O_2^{•-} \rightarrow OH^• + O_2 + OH^- \qquad (4.9)$$

Photogenerated hydrogen peroxide (H_2O_2) and its addition to the photocatalytic system increase the photodegradation efficiency because it can additionally absorb radiation and directly form $OH^•$ radicals (Eq. 4.10). H_2O_2 can also accept the conduction band e^-_{cb} to generate $OH^•$ radicals (Eq. 4.11) thus prevents e^-_{cb}/h^+_{vb} recombination and increases the availability and life of valence band holes [15, 17, 21].

$$H_2O_2 + hv \rightarrow OH^• + OH^• \qquad (4.10)$$

$$H_2O_2 + e^-_{cb} \rightarrow OH^• + OH^- \qquad (4.11)$$

$$OH^• + Contaminants \rightarrow Intermediates \qquad (4.12)$$

$$OH^• + Intermediates \rightarrow CO_2 + H_2O + Endproducts \qquad (4.13)$$

Figure 4.1 shows the photo-excitation of a TiO_2 solid particle by light radiation, charge separation, generation of e^-_{cb}/h^+_{vb} pair, charge transport, and oxidation-reduction reactions at the surface. X is an oxidant and Y is a reductant. Thus, the photo-excited TiO_2 surface is an attractive catalyst for the degradation of almost all organic contaminants including chlorophenolics [13, 22, 25-27].

This chapter investigates the optimization of process parameters and photocatalytic degradation of the pulp bleaching and paper mill effluents using TiO_2 photocatalysis. Additionally, catalyst characterization, recycling, treatment process efficiency, and economic feasibility studies have also been performed. The photocatalytic oxidation experiments were conducted under UV or solar radiation.

4.3 RESULTS AND DISCUSSION

4.3.1 Catalyst characterization

4.3.1.1 XRD and FE-SEM analysis

XRD pattern of TiO_2 (Figure 4.2) depicts peaks at 2θ = 25.53, 37.17, 38.01, 38.77, 48.25, 54.10, and 55.27° which correspond to the different diffraction planes of anatase phase. A very small peak at $2\theta = 27.68°$ can be attributed to the diffraction plane of rutile phase which is much smaller than those of anatase. The results show that the major phase of TiO_2 is anatase. These findings agree with the observations in a number of earlier reports (Table 4.1). TiO_2 powder was found to be composed of mainly anatase (99.97 wt%) and small fraction of rutile (0.03 wt%) as supported by XRD data. FE-SEM images show that TiO_2 is composed of nano-sized particles with spherical or near-spherical morphology (Figure 4.3). TiO_2 particle size was found to be in the range of 50-150 nm.

4.3.1.2 FTIR analysis

FTIR spectrum of TiO_2 (Figure 4.4) shows a broad peak associated with the characteristic vibrational modes of TiO_2 in the range of 400-1000 cm^{-1} which corresponds to Ti-O and Ti-O-Ti stretching vibrations of the crystalline anatase and rutile phases. The large peak at 3100-3600 cm^{-1} is in the hydroxyl stretching region and should correspond to O-H vibration of Ti-OH groups and adsorbed H_2O molecules with characteristic peaks at 3494 cm^{-1} and 3440 cm^{-1}, respectively. The binding vibration H-O-H at 1592 cm^{-1} and stretching vibration O-H at 3398 cm^{-1} indicate existence of small amount of surface-adsorbed molecular water and hydroxyl groups. FTIR peaks observed are comparable with those reported in the literature (Table 4.2).

4.3.1.3 EDX and S_{BET} analysis

EDX spectrum of TiO_2 (Figure 4.5) depicts three distinct X-ray lines associated with O Kα (0.512), Ti Kα (4.519), and K_β (4.962). These results indicate that Ti and O are the constitutive elements of the nano-particles with 80.33 and 19.67 wt%, respectively. These findings are consistent with those reported earlier [28, 29]. Surface area (S_{BET}) and total pore volume were determined to be on the order of 26.1 m^2/g and 0.01 m^3/g, respectively.

4.3.2 Optimization of photocatalytic treatment parameters

The paper mill primary clarified (PC) effluent was used for the optimization studies. The analytical characteristics of PC effluent are depicted in Table 4.3. The effluent should have initial chemical oxygen demand (COD) below 800 mg/L for successful catalysis because excess of the organic matter tends to cover the catalyst surface through adsorption. The suspended particulate matter causes scattering of light radiation and reduces the amount of photons reaching the photoactive sites of the catalyst [17]. Initial COD of PC effluent was 900 mg/L. Hence, it was diluted to bring COD value to approximately 500 mg/L for all the experiments.

Some blank experiments were performed to study the effect of ultra violet (UV) radiation and physical adsorption of organics on TiO_2 surface on COD removal efficiency. The effluent was treated with UV radiation, TiO_2, and UV/TiO_2 process, respectively, at a pH 7.0 for 4 h. When the effluent sample was irradiated in the absence of TiO_2 there was no significant COD (4%) removal, while 10% COD removal was obtained with non-irradiated reaction mixture containing the catalyst. This may be due to the dark adsorption of organic matter on the catalyst surface [18]. The adsorption of pollutants on the catalyst surface is important because the photogenerated h^+_{vb} on the catalyst surface can either directly oxidize the pollutants or by generating $OH^•$ radicals [23]. When both were used together, i.e. UV/TiO_2 process, 47% COD removal was achieved (Figure 4.6). Thus, neither UV photolysis nor TiO_2 alone is the significant mechanism for the degradation of organic matter present in the paper mill effluent. Thus degradation of pollutants is due to the combined process of physical adsorption and photocatalysis.

4.3.2.1 Catalyst dose optimization

The catalyst dose was optimized by varying TiO_2 concentration from 0.25 to 1.5 g/L at a pH 7.0 and irradiating for 4 h. The percentage COD and color removal increased as the catalyst concentration increased from 0.25 to 0.75 g/L (Figure 4.7 a). However, once TiO_2 concentration exceeded 0.75 g/L, color and COD removal efficiency decreased. An excess concentration of catalyst causes turbidity and scattering of light radiation thus decreases the light penetration into the reaction mixture. The generation of charge carriers is affected, resulting in reduced photodegradation efficiency [17, 30, 31]. We obtained maximum removal of COD (55%) and color (84%) at a catalyst dose of 0.75 g/L, while at 0.5 g/L of TiO_2, COD and color removal was 50 and 78%, respectively. Thus, it is clear that there is not much increase in degradation efficiency when TiO_2 dose is increased from 0.5 to 0.75 g/L. Hence, 0.5 g/L of TiO_2 was selected as the optimum catalyst loading for subsequent studies.

4.3.2.2 pH optimization

To determine the optimum pH suitable for UV/TiO_2 treatment of paper mill effluent various experiments were performed at different solution pH (3.0 to 8.0), by using 0.5 g/L of TiO_2 for 4 h (Figure 4.7 b). The maximum COD (63%) removal and decolorization (92%) was achieved at acidic pH (3.0). At neutral pH (7.0), 46% COD and 75% color removal was obtained. At slightly alkaline pH (8.0), 46% COD and 68% color removal was obtained. We obtained more COD and color removal at pH 7.0 as compared to pH 8.0. The natural pH of the paper mill PC effluent varied from 7.1 to 7.9 hence we selected pH 7.0 as optimum for further studies. pH is an important parameter in the photocatalysis. It governs the catalyst charge and affects the adsorption of organics onto the catalyst surface and particle aggregation [32]. The catalyst surface is positively charged in the acidic pH and negatively charged in the alkaline medium. At acidic pH, the positively charged catalyst surface allows adsorption of H_2O/OH^- ions (generating $OH^•$ radicals) and organic pollutants by intermolecular and surface charge interactions. The paper mill effluent is characterized with anionic organic pollutants having negative groups hence they get adsorbed on the positively charged catalyst surface and react with radicals [17]. At alkaline pH, there is repulsion between the negatively charged catalyst surface and OH^- ions/anionic pollutants hence a reduction in photodegradation efficiency results.

4.3.2.3 Reaction time optimization

The optimization of the reaction time was done by following the percentage removal in COD and color of the effluent during the course of the reaction at definite intervals of time (0.5 to 8 h) at a pH 7.0 with 0.5 g/L of TiO_2. A rapid decrease in effluent COD and color was observed during the first 1 h of treatment (Figure 4.7 c). Tanaka et al. [33] reported a high rate of degradation for TiO_2 photocatalysis within a short period of time leading to complete oxidation of organics. After 1 h, the rate of degradation slows down and after a particular time period (4 h) it becomes more or less constant. This observation may be explained by the fact that paper mill effluent is characterized by a large concentration of organics. Hence, a nearly constant concentration of contaminants is available for photodegradation during the initial phase of the reaction [18]. After this initial phase, the rate of degradation decreases that may be due to the adsorption of organic matter on to TiO_2 surface that forms a layer which hinders the photodegradation by diminishing the supply of oxygen to the catalyst surface [15]. In addition to pH change of the solution, a decrease in concentration of pollutants, ageing of the catalyst, competition for surface active sites between the pollutants and reaction intermediates, and the formation of catalyst agglomerates contribute to a reduction in photocatalysis [18]. After 4 h of reaction, 54 and 82% COD and color removal, respectively, was achieved. Increasing the reaction time to 8 h did not significantly increase the degradation efficiency. Hence, 4 h reaction time was selected as optimum for subsequent experiments.

4.3.2.4 Light intensity optimization

The amount of light radiation reaching to the reaction mixture was varied by changing the distance (8 to 43 cm) between UV lamp and the surface of the reaction mixture. The effect of light intensity on COD and color removal efficiency was studied by irradiating at a pH 7.0 with 0.5 g/L of TiO_2 for 4 h. The highest COD (45%) and color removal (77%) was obtained at a distance of 15 cm (Figure 4.7 d). When the distance was increased or decreased beyond 15 cm the degradation efficiency decreased. It means that at 15 cm we obtained the optimum light intensity (2.28×10^{-6} q_{np}/Einstein s^{-1}). The light intensity as well as the degradation efficiency declined with increasing distance from the light source. Light intensity is an important parameter and the rate of photocatalytic degradation is dependent on light intensity. At high intensity levels, the effluent degradation reaction rate increases with the square root of the light intensity but becomes a first order function at lower intensity levels [8].

4.3.2.5 Organic load optimization

The initial organic load in the effluent is an important parameter in the heterogeneous photocatalysis. To study the effect of initial organic load, effluent was diluted in different ratios. The rate of photodegradation decreased as the initial COD value increased (Figure 4.7 e). For initial COD values of 995, 570, and 325 mg/L, after 4 h of irradiation at pH 7.0 and catalyst loading of 0.5 g/L, 18, 45, and 59% COD removal, respectively, was achieved. As the initial organic load increases, the amount of organic matter adsorbed onto the catalyst surface increases. This decreases the amount of light photons reaching the catalyst surface and the relative amount of oxidizing species on the catalyst surface does not increase as the intensity and time of illumination remain constant, thus decreasing the photodegradation rate [8].

4.3.2.6 Oxidant concentration optimization

The effect of initial oxidant concentration on photodegradation efficiency was investigated by experimenting with different concentrations of H_2O_2 (5 to 75 mM/L) at pH 7.0 and the optimum TiO_2 dose previously determined as 0.5 g/L. There is a sharp increase in the degradation rate up to 15 mM/L of H_2O_2 concentration (Figure 4.7 f). With further addition of peroxide (25 mM/L), there is only a minor increase in the degradation rate and thereafter (50 and 75 mM/L) the rate is essentially constant. An excess concentration of H_2O_2 is likely to absorb light radiation for its photolysis, thus reducing the amount of radiation available for TiO_2 photo-excitation and it may react with the $OH^{\bullet}$ radicals to produce hydroperoxyl radicals [17]. Thus, high concentration of H_2O_2 depresses the photocatalysis by reducing the amount of $OH^{\bullet}$ radicals available for photodegradation. There is a small increase in photodegradation efficiency when going from 15 mM/L (59% COD and 90% color removal) to 25 mM/L of H_2O_2 (65% COD and 95% color removal). The increase in degradation efficiency is not proportional to the increase in H_2O_2 concentration. Hence, 15 mM/L of H_2O_2 was selected as the optimized value for further treatment studies. Addition of H_2O_2 enhanced the photocatalysis efficiency. These findings are in concordance with those reported in the literature [19, 34].

4.3.2.7 Reaction temperature optimization

All the photocatalytic degradation experiments were performed at ambient temperature. During the heterogeneous photocatalytic degradation of pollutants, the exothermic recombination of e^-_{cb}/h^+_{vb} pairs also occurs releasing the absorbed light energy as heat. The light source used for the photocatalysis also generates heat radiation. Thus, the temperature of the reaction mixture might increase [31]. Hence, some experiments were also performed for studying the effect of temperature on the photodegradation efficiency. The effluent was treated under optimized conditions by UV/TiO_2 process at two different reaction temperatures (25 °C and 50 °C) and the removal in COD was monitored to examine the effect on photodegradation reaction efficiency. There was not a significant increase in degradation efficiency when the temperature was raised from 25 °C (46% COD removal) to 50 °C (49% COD removal). Thus, reaction temperature is not a significant reaction variable in heterogeneous photocatalysis. A weak dependence of the degradation rate on temperature has been reported in the range of 20 °C to 80 °C [21, 31].

Catalyst dose, pH, reaction time, organic loading, and light intensity were the significant parameters affecting the rate of photodegradation. No significant effect of reaction temperature on the degradation efficiency was observed. The addition of H_2O_2 to the UV/TiO_2 process enhanced the photodegradation efficiency. The best experimental conditions obtained are: pH 7.0, TiO_2 dose 0.5 g/L, H_2O_2 dose 15 mM/L, and reaction time of 4 h.

4.3.3 Pulp bleaching effluent treatment

4.3.3.1 Characteristics of effluents

The average analytical characteristics of pulp bleaching effluents are summarized in Table 4.4. DED sequence effluents presented high organic load in terms of biochemical oxygen demand (BOD) and COD as compared to D/CED, DE_PD, and ODED sequences. The highest amount of AOX, chlorophenolics, and chloro-resin and fatty acids (cRFA) was present in D/CED sequence effluents followed by DED, DE_PD, and ODED (Tables 4.4, 3.5-3.8, 3.10). D_1 stage effluents of all the sequences except D/CED (D/C stage: conducted at lower consistency) were characterized with higher COD load as compared to E or E_P and D_2 stages. While E or E_P stage effluents were characterized with high color as compared to D/C or D_1 and D_2 stages of all the bleaching sequences. E stage effluent of D/CED sequence was having highest amount of color followed by DED, DE_PD, and ODED sequences. ODED sequence effluents presented lowest pollution load as compared to other sequences. BOD/COD ratio of the effluents was low indicating low biodegradability of the organics present in the effluents. The lowest BOD/COD ratio was observed for D/CED sequence effluents followed by DED, DE_PD, and ODED sequences. These findings are in accordance with the concentration of AOX, chlorophenolics, and cRFA present in the effluents. The first two bleaching stages (D/C or D_1, and E or E_P) were the major source of pollution load in the effluent. Hence we focussed our study to the photocatalytic degradation of pollutants from the effluents of only these stages.

The presence of chlorinated organics and lower BOD/COD ratio renders these effluents unsuitable for biological degradation because they may affect development of microorganisms and thus efficiency of biological degradation. Hence, there is a need for advanced chemical oxidation for degrading biorefractory organics. D_1 (DED and DE_PD sequences) and E (D/CED, DED, and DE_PD sequences) stage effluents were diluted to bring the initial COD values to 500 mg/L before photocatalysis. ODED sequence effluents and D/C stage effluent of D/CED sequence were used directly for photodegradation studies. The photocatalytic treatment has been investigated under optimized conditions (pH 7.0, TiO_2 dose 0.5 g/L, H_2O_2 dose 15 mM/L, and reaction time of 4 h) using UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes.

4.3.3.2 COD removal

COD is a measure of oxygen demanding organic or inorganic material dissolved in the effluent [20]. degradation of organic matter present in the effluents was studied in terms of percentage COD removal. After 4 h of treatment, 62, 63, 65, and 73% COD removal for D/C or D_1 stage effluents of D/CED, DED, DE_PD, and ODED sequences, respectively, by $UV/TiO_2/H_2O_2$ process was achieved. This was higher as compared to UV/TiO_2 process (Figure 4.8 a). The higher COD removal for D_1 stage effluent of ODED sequence is due to presence of initially very low color (121.8 mg/L) and slightly lower COD (430.8 mg/L) (Table 4.4) as compared to DED and DE_PD sequences (500 mg/L COD for treatment). For D/C stage effluent of D/CED sequence slightly lower COD removal was observed in spite of initial lower color (353 mg/L) and COD (371 mg/L) as compared to DED and DE_PD sequences. This may be due to the presence of initially higher concentration of AOX (58 mg/L) as compared to other bleaching sequences. While for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences, 43, 66, 70, and 76% COD removal, respectively, was achieved by $UV/TiO_2/H_2O_2$ process which was higher as compared to UV/TiO_2 process (Figure 4.9 a). The highest COD removal efficiency was observed for ODED sequence effluents as compared to D/CED, DED, and DE_PD sequences. The difference in COD removal efficiency for different effluents may be due to the difference in the molecular weights and structure of the dissolved organic pollutants present in the effluents [19]. E or E_P stage effluents of DED, DE_PD, and ODED sequences were more amenable to photodegradation as compared to D_1 stage effluents. While in case of D/CED sequence higher COD removal was achieved for D/C stage effluents due to initial low color load as compared to E stage.

4.3.3.3 BOD removal

A noticeable removal of BOD was observed for all the effluents, probably due to the photochemical degradation of the biodegradable species [35]. Higher BOD removal efficiency was achieved with $UV/TiO_2/H_2O_2$ process compared to UV/TiO_2 process. $UV/TiO_2/H_2O_2$ process removed BOD up to 47, 44, 45, and 51% for D/C or D_1 stage and 20, 49, 54, and 60% for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences, respectively (Figure 4.8 b and 4.9 b). These results are in accordance with those reported earlier [35, 36]. The biodegradability of the pollutants present in the effluents was estimated in terms of improvement in BOD/COD ratio of effluents after photocatalytic oxidation. The initial biodegradability index of the effluents was low, i.e. 0.21, 0.24, 0.26, and 0.28 for D/C or D_1 stage and 0.19, 0.24, 0.25, and 0.29 for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences, respectively. For complete biodegradation, the effluent must have a biodegradation index of at least 0.4 [37]. BOD/COD ratio improved to 0.29, 0.37, 0.41, and 0.51 for D/C or D_1 stage and 0.26, 0.36, 0.38, and 0.48 for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences, respectively, by $UV/TiO_2/H_2O_2$ process which is higher as compared to UV/TiO_2 process (Figures 4.10 a and b). These findings are in good agreement with the literature that TiO_2 photocatalysis improves the biodegradability of the organic matter present in the effluents [38]. For D_1 and E stage effluents of ODED sequence and D_1 stage effluent of DE_PD sequence, BOD/COD ratio increased over the optimal value (0.4) after treatment by $UV/TiO_2/H_2O_2$ process. These findings indicate easy removal of pollutants in biological treatment plant.

4.3.3.4 Color removal

The brown color of the bleaching effluents is primarily due to the presence of lignin and it's derivatives (high molecular weight substances) that are released from the substrate during bleaching [39]. The color removal, after 4 h of treatment, achieved was 95, 91, 92, and 98% for D/C or D_1 stage and 76, 89, 90, and 97% for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences, respectively, by $UV/TiO_2/H_2O_2$ process. This was higher as compared to UV/TiO_2 process (Figures 4.8 c and 4.9 c). For ODED sequence effluents the highest color removal was achieved as compared to other sequences. O_2 delignification decreases the color of effluents by 63-80% [40]. Hence, the color of ODED sequence effluents was already very low as compared to D/CED, DED, and DE_PD sequences. This resulted in higher removal efficiency. Heterogeneous photocatalysis has been reported to be the most efficient for the discoloration of effluents [36]. Higher color removal was achieved for D/C or D_1 stage effluents as compared to E or E_P stage effluents. E or E_P stage effluents were having initially high color load as compared to D/C or D_1 stage effluents, hence lower decolorization efficiency was observed (Table 4.4).

4.3.3.5 AOX removal

AOX is an approximate measure of the chlorinated organics present in the pulp bleaching effluents and toxicity, which must be reduced in any effluent treatment system [41]. After 4 h of treatment, AOX removal achieved was 23, 49, 54, and 64% for D/C or D_1 stage and 35, 57, 58, and 67% for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences, respectively, by $UV/TiO_2/H_2O_2$ process which is higher as compared to UV/TiO_2 process (Figure 4.8 d and 4.9 d). For D/C and E stage effluents of D/CED sequence lowest AOX removal was observed due to the presence of initially high AOX and color load, respectively as compared to other sequences (Table 4.4). Yeber et al. [42] while treating eucalyptus E_1 stage effluent using immobilized catalyst observed 85 and 90% removal of AOX after 60 and 120 minutes of treatment, respectively. They emphasized that the high removal in a short period of treatment must be a consequence of the high irradiation power of the lamp. In our case the low removal efficiencies may be due to the low irradiation power of the lamps. As the lamp power (light intensity) increases, the rate of e^-/h^+ pair formation at TiO_2 surface increases and as a result its ability to oxidize organic pollutant [9]. The highest AOX removal was achieved for ODED sequence effluents and the lowest for D/CED sequence effluents. This is due to initially low AOX and organic load of ODED sequence effluents as compared to effluents of other sequences. The higher AOX removal was achieved for E or E_P stage effluents as compared to D/C or D_1 stage effluents for all bleaching sequences. E or E_P stage effluents were having lower concentration of AOX and COD (except D/CED sequence) as compared to D/C or D_1 stage effluents of all bleaching sequences, hence higher removal efficiency was observed (Table 4.4).

$UV/TiO_2/H_2O_2$ process was found to be more effective for the photodegradation of pollutants from pulp bleaching effluents as compared to UV/TiO_2 process. The higher removal efficiency was achieved for ODED sequence effluents followed by DE_PD, DED, and D/CED sequences. ODED sequence effluents were more amenable to photocatalytic degradation due to initially very low color and pollution load as compared to effluents of other sequences. Significant color removal efficiency was achieved by both the processes. Photocatalysis increased the biodegradability of the pollutants present in the pulp bleaching effluents, which can be further degraded by biological processes, and improved water quality.

4.3.3.6 Chlorophenolics removal

(a) Chlorophenolics removal for D/CED sequence effluents

For D/C stage, 37% removal of chlorophenolics was achieved by UV/TiO_2 process (Table 4.5). CV were removed to the maximum extent (73%) followed by CSA (53%), CG (51%), CP and CS (39%), and CC (22%). CP were removed in the range of 29-100%. 2,3-DCP, 2,3,6-TCP, and 2,4,6-TCP were not detected in the effluent. 3-CP was removed up to the maximum extent (83%) followed by 3,4-DCP (82%), 2,3,4-TCP (80%), 2,6-DCP (78%), 4-CP (76%), and 2,3,5-TCP (69%). PCP, most toxic of the group, was removed up to 61%. The remaining CP were removed up to 42%. CG were removed in the range of 45-77%. 4-CG (77%) and 4,5,6-TCG (70%) were removed up to the maximum extent. The remaining CG were degraded up to 56%. Among CC, 3,5-DCC was removed to the maximum extent (62%) followed by Tet-CC (56%) and 3,6-DCC (17%). Among other chlorophenolics, 5,6-DCV was removed to the highest extent (73%) followed by 2,6-DCSA (53%) and TCS (39%) (Table 4.5).

MCP were removed to the highest extent (80%) followed by PCP (61%), Tet-CP (50%), TCP (43%), and DCP (31%) (Figure 4.11 b). UV/TiO_2/H_2O_2 process removed 44% chlorophenolics (Table 4.5). CV was removed to the maximum extent (82%) followed by CG (58%), CSA (56%), CP (45%), CS (42%), and CC (31%) (Figure 4.11 a). CP were removed in the range 37-100%. 2,6-DCP, 2,3-DCP, 2,3,6-TCP, and 2,4,6-TCP were not detected in the effluent. 4-CP was removed to the maximum extent (89%) followed by 3,4-DCP (87%), 3-CP (85%), 2,3,4-TCP (82%), and 2,3,5-TCP (80%). PCP was removed up to 68%. The remaining CP were removed up to 51%. CG were removed in the range of 53-81%. 4-CG (81%) and 4,5,6-TCG (73%) were removed up to the maximum extent. The remaining CG were degraded up to 61%. Among CC, 3,5-DCC was removed to the maximum extent (67%) followed by Tet-CC (58%), and 3,6-DCC (26%). Among other chlorophenolics, 5,6-DCV was removed to the highest extent (83%) followed by 2,6-DCSA (57%), and TCS (42%) (Table 4.5). MCP were removed to the highest extent (85%) followed by PCP (68%), Tet-CP (54%), TCP (47%), and DCP (39%) (Figure 4.11 b).

For E stage effluent, UV/TiO_2 process removed 18% chlorophenolics (Table 4.5). CV were removed to the maximum extent (43%) followed by CC (33%), CSA (21%), CG (19%), CP (14%), and CS (13%) (Figure 4.11 c). CP were removed in the range 8-100%. 2,3,6-TCP was not detected in the effluent after treatment. 3,4-DCP was removed up to the maximum extent (73%) followed by 2,3,5-TCP (69%), 2,4,6-TCP (68%), and 2,3-DCP (63%). The remaining CP were removed up to 48. CG were removed in the range of 12-42%. 4-CG (42%) and 4,5,6-TCG (39%) were removed up to the maximum extent. The remaining CG were removed up to 30. Among CC, Tet-CC was removed to the maximum extent (50%) followed by 3,5-DCC (46%) and 3,6-DCC (29%). Among other chlorophenolics, 5,6-DCV was removed to the highest extent (43%) followed by 2,6-DCSA (21%), and TCS (13%) (Table 4.5). PCP was not detected after treatment. MCP were removed up to 41% followed by Tet-CP (33%), DCP (18%), and TCP (15%) (Figure 4.11 d). UV/TiO_2/H_2O_2 process removed 25% chlorophenolics (Table 4.5). CV was removed to the maximum extent (49%) followed by CC (39%), CSA (30%), CG (26%), CS (25%), and CP (21%) (Figure 4.11 c). CP were removed in the range of 11-100%. 2,3,6-TCP was not detected in the effluent after treatment. 2,3-DCP was removed to the highest extent (89%) followed by 3,4-DCP (87%), 2,4,6-TCP (80%), and 2,3,5-TCP (74%).

The remaining CP were removed up to 59%. CG were removed in the range of 17-49%. 4-CG (49%) and 4,5,6-TCG (42%) were removed up to the maximum extent. The remaining CG were removed up to 37%. Among CC, Tet-CC was removed to the maximum extent (52%) followed by 3,5-DCC (48%) and 3,6-DCC (36%). Among other chlorophenolics, 5,6-DCV was removed to the highest extent (49%) followed by 2,6-DCSA (30%) and TCS (25%) (Table 4.5). PCP was not detected after treatment. MCP were removed up to 51% followed by Tet-CP (37%), DCP (24%), and TCP (25%) (Figure 4.11 d).

(b) Chlorophenolics removal for DED sequence effluents

For D_1 stage effluent, 55% removal of chlorophenolics was achieved by UV/TiO_2 processes (Table 4.6). CS was not detected after treatment. CP were removed up to 82% followed by CV (71%), CC (62%), CSA (60%), and CG (47%) (Figure 4.12 a). CP were removed in the range of 73-100%. 2,3-DCP and 2,4,6-TCP were not detected in the effluent. PCP was removed up to the maximum extent (97%) followed by 3-CP (90%), 2,5-DCP, 2,4-DCP, and 2,4,5-TCP (82%). The remaining CP were removed up to 79%. CG were removed in the range of 43-100%. 3,4,6-TCG and 4,5,6-TCG were not detected in the effluent after treatment. 4,6-DCG was removed to the maximum extent (88%) followed by 3,4,5-TCG (80%) and Tet-CG (76%). The remaining CG were removed up to 54%. Among CC, 3,5-DCC was removed to the maximum extent (77%) followed by Tet-CC (74%) and 3,6-DCC (56%). Among other chlorophenolics, TCS was not detected. 5,6-DCV was removed up to 71% and 2,6-DCSA 60% (Table 4.6). PCP was removed up to 97%. TCP was removed up to 82% followed by Tet-CP (74%), MCP (61%), and DCP (51%) (Figure 4.12 b). While UV/TiO_2/H_2O_2 process removed 63% removal of chlorophenolics (Table 4.6). CS was not detected after treatment. CP were removed to the maximum extent (90%) followed by CV (84%), CC (70%), CSA (67%), and CG (54%) (Figure 4.12 a). CP were removed in the range of 82-100%. 2,4-DCP, 2,3-DCP, 2,4,6-TCP, and PCP were not detected in the effluent. 2,3,6-TCP was removed to the maximum extent (94%) followed by 3-CP (93%), 2,3,4-TCP (91%), and 4-CP (89%). The remaining CP were removed up to 88%. CG were removed in the range of 51-100%. 3,4,6-TCG and 4,5,6-TCG were not detected in the effluent after treatment. 4,6-DCG was removed to the maximum extent (95%) followed by 3,4,5-TCG (86%) and Tet-CG (86%). The remaining CG were removed up to 62%. Among CC, 3,5-DCC was removed to the maximum extent (88%) followed by Tet-CC (83%) and 3,6-DCC (64%). Among other chlorophenolics, TCS was not detected after treatment. 5,6-DCV was removed up to 84% and 2,6-DCSA 67% (Table 4.6). PCP was not detected after treatment. TCP was removed up to 91% followed by Tet-CP (84%), MCP (69%), and DCP (59%) (Figure 4.12 b).

For E stage effluent, chlorophenolics were removed up to 48% by UV/TiO_2 process (Table 4.6). CC were removed to the maximum extent (68%) followed by CV (65%), CP (50%), CG (45%), and CSA (30%) (Figure 4.12 c). CP were removed in the range of 41-100%. 2,6-DCP was not detected after treatment. 2,4-DCP was removed up to the maximum extent (90%) followed by 2,5-DCP (88%), 2,4,6-TCP (83%), and 2,3-DCP (82%). The remaining CP were removed up to 78%. CG were removed in the range of 40-84%. 4,6-DCG was removed to the maximum extent (84%) followed by Tet-CG (71%), 3,4,6-TCG (70%), and 3,4,5-TCG (68%). The remaining CG were removed up to 63%. Among CC, 3,5-DCC was removed to the maximum extent (80%) followed by Tet-CC (69%) and 3,6-DCC (63%). Among other chlorophenolics, 5,6-DCV was removed up to 65% and 2,6-DCSA 30% (Table 4.6). PCP was removed to the highest extent (74%) followed by TCP (70%), Tet-CP (69%), MCP (47%), and DCP (47%) (Figure 4.12 d). While UV/TiO_2/H_2O_2 process removed chlorophenolics up to 57% (Table 4.6). CC were removed to the maximum extent (75%) followed by CV (66%), CP (57%), CG (55%), and CSA (37%) (Figure 4.12 c). CP were removed in the range of 48-100%. 2,6-DCP, 2,3-DCP, 2,4,6-TCP, and 2,3,4-TCP were not detected after treatment. 2,4-DCP was removed to the maximum extent (95%) followed by 2,5-DCP (92%), PCP (82%), and 2,4,5-TCP (81%). The remaining CP were removed up to 69%. CG were removed in the range of 52-94%. 4,6-DCG was removed to the maximum extent (94%) followed by Tet-CG (77%), 3,4,6-TCG (74%), and 3,4,5-TCG (88%). The remaining CG were removed up to 70%. Among CC, 3,5-DCC was removed to the maximum extent (86%) followed by Tet-CC (73%) and 3,6-DCC (72%). Among other chlorophenolics, 5,6-DCV was removed up to 66% and 2,6-DCSA 37% (Table 4.6). PCP was removed to the highest extent (82%) followed by TCP (81%), Tet-CP (74%), MCP (56%), and DCP (57%) (Figure 4.12 d).

(c) Chlorophenolics removal for DE$_P$D sequence effluents

For D_1 stage effluent, UV/TiO_2 removed chlorophenolics up to 57% (Table 4.7). CP were removed to the maximum extent (87%) followed by CC (66%) and CG (50%) (Figure 4.13

a). CP were removed in the range of 77-93%. 2,5-DCP was removed up to the maximum extent (93%) followed by 3-CP (92%), 2,6-DCP and 2,4,5-TCP (86%), and 2,4-DCP (84%). The remaining CP were removed up to 81%. Among the identified CG, 4,6-DCG was not detected after treatment. 3,4,5-TCG was removed up to maximum extent (82%) followed by 4-CG (58%) and 4,5-DCG (47%). Among CC, 3,5-DCC was removed up to 83% followed by Tet-CC (83%) and 3,6-DCC (59%). TCP were removed to the highest extent (83%) followed by Tet-CP (83%), MCP (60%), and DCP (55%) (Figure 4.13 b). While UV/TiO_2/H_2O_2 process removed chlorophenolics up to 64% (Table 4.7). CP were removed to the maximum extent (92%) followed by CC (73%) and CG (57%) (Figure 4.13 a). CP were removed in the range of 79-100%. 2,6-DCP was not detected in the effluent after treatment. 3-CP was removed to the highest extent (97%) followed by 4-CP (96%), 2,4,5-TCP and 2,3,4-TCP (93%), and 2,4-DCP (91%). The remaining CP were removed up to 89%. Among the identified CG, 4,6-DCG and 3,4,5-TCG were not detected after treatment. 4-CG was removed up to 65% and 4,5-DCG up to54%. Among CC, 3,5-DCC was removed up to 91% followed by Tet-CC (88%) and 3,6-DCC (66%). TCP were removed to the highest extent (93%) followed by Tet-CP (88%), MCP (68%), and DCP (62%) (Figure 4.13 b).

For E_P stage effluent, chlorophenolics were removed up to 53% after treatment by UV/TiO_2 process (Table 4.7). CC were removed up to 90%. CSA was removed up to 83% followed by CV (74%), CP (68%), and CG (49%) (Figure 4.13 c). CP were removed in the range of 56-92%. 2,4-DCP was removed up to the maximum extent (92%) followed by 2,5-DCP (89%), 4-CP and 2,4,5-TCP (87%), and 2,3,4-TCP (84%). The remaining CP were removed up to 75%. Among CG, 4,5,6-TCG was not detected after treatment. 4,6-DCG was removed up to 90% followed by 4-CG (52%) and 4,5-DCG (46%). Among other chlorophenolics, Tet-CC was removed up to 90% followed by 2,6-DCSA (83%) and 5,6-DCV (74%). Tet-CP were removed up to 90%. TCP were removed up to 90% followed by MCP (53%) and DCP (52%) (Figure 4.13 d). While UV/TiO_2/H_2O_2 process removed chlorophenolics up to 61% (Table 4.7). CC were not detected after treatment. CSA was removed up to 86% followed by CV (78%), CP (74%), and CG (57%) (Figure 4.13 c). CP were removed in the range of 64-100%. 4-CP and 2,4-DCP were not detected in the effluent after treatment. 2,4,5-TCP was removed to the maximum extent (97%) followed by 2,3,4-TCP (95%) and 2,5-DCP (92%). The remaining CP were removed up to 81%. Among CG, 4,5,6-TCG was not detected after treatment. 4,6-DCG was removed up to 95% followed by 4-CG (59%) and 4,5-DCG (55%). Tet-CC and Tet-CP were not detected after treatment. 2,6-DCSA was removed up to 86% and 5,6-DCV up to 78%. TCP were removed up to 97% followed by MCP and DCP (60%) (Figure 4.13 d).

(d) Chlorophenolics removal for ODED sequence effluents

For D_1 stage effluent, UV/TiO_2 process removed chlorophenolics up to 66% (Table 4.8). CSA was removed up to 86%. CG were removed up to 84% followed by CP (75%), CV (65%), and CC (59%) (Figure 4.14 a). CP were removed in the range of 69-100%. 2,4,6-TCP was not detected in the effluent after treatment. 2,6-DCP and 2,5-DCP were removed up to the maximum extent (88%) followed by 4-CP (85%), 2,4-DCP (83%), and 3-CP (81%). The remaining CP were removed up to 80%. Among the identified CG, 3,4,5-TCG and 4,6-DCG were not detected after treatment. 3,4,6-TCG was removed up to 91%. 4-CG was removed up to 87% and 4,5-DCG up to 80%. Among CC, Tet-CC was removed up to the maximum extent (84%) followed by 3,5-DCC (61%) and 3,6-DCC (55%) (Table 4.8). Among other chlorophenolics, 2,6-DCSA was removed up to 86%. 5,6-DCV was removed up to 65%. Tet-CP was removed up to 84% followed by MCP (85%), TCP (75%), and DCP (62%) (Figure 4.14 b). While UV/TiO_2/H_2O_2 process removed chlorophenolics up to 74% (Table 4.8). CSA was not detected after treatment. CG were removed up to 92% followed by CP (83%), CV (73%), and CC (66%) (Figure 4.14 a). CP were removed in the range of 76-100%. 2,4,6-TCP was not detected in the effluent after treatment. 4-CP was removed to the maximum extent (97%) followed by 2,5-DCP (93%), 2,6-DCP (91%), 2,4-DCP and 2,3,4-TCP (86%), and 3-CP (85%). The remaining CP were removed up to 81%. Among the identified CG, 3,4,5-TCG, 3,4,6-TCG, and 4,6-DCG were not detected after treatment. 4-CG was removed up to 94% and 4,5-DCG up to 89%. Among CC, Tet-CC was removed up to the maximum extent (96%) followed by 3,5-DCC (68%) and 3,6-DCC (61%) (Table 4.8). Among other chlorophenolics, 2,6-DCSA was not detected after treatment. 5,6-DCV was removed up to 73%. Tet-CP were removed up to 96% followed by MCP (92%), TCP (84%), and DCP (69%) (Figure 4.14 b).

For E stage effluent, chlorophenolics were removed up to 42% after treatment by UV/TiO_2 process (Table 4.8). CC and CS were not detected after treatment. CSA was removed up to 84% followed by CP (73%), CV (65%), and CG (34%) (Figure 4.14 c). CP were removed in the range of 65-100%. 2,3-DCP was not detected in the effluent after treatment. 4-CP was removed up to the maximum extent (96%) followed by 2,3,5-TCP (92%), 3-CP (86%), 2,6-DCP and 2,3,6-TCP (82%). The remaining CP were removed up to 79%. Among the identified CG, 4,6-DCG was removed to the highest extent (84%) followed by 4-CG (56%) and 4,5-DCG (28%). Among remaining chlorophenolics, Tet-CC and TCS were not detected after treatment. 2,6-DCSA was removed up to 84% and 5,6-DCV up to 65%. Tet-CP were not detected in the effluent after photocatalysis. TCP were removed up to 74% followed by MCP (58%) and DCP (32%) (Figure 4.14 d). While UV/TiO_2/H_2O_2 process removed chlorophenolics up to 49% (Table 4.8). CC and CS were not detected after treatment. CSA was removed up to 93% followed by CP (82%), CV (68%), and CG (41%) (Figure 4.14 c). CP were removed in the range of 70-100%. 4-CP, 2,3-DCP, 2,3,6-TCP, and 2,3,5-TCP were not detected in the effluent after treatment. 3-CP was removed to the maximum extent (89%) followed by 2,6-DCP (86%), 2,5-DCP (85%), and 2,4-DCP (84%). The remaining CP were removed up to 77%. Among the identified CG, 4,6-DCG was removed to the highest extent (95%) followed by 4-CG (60%) and 4,5-DCG (35%). Among remaining chlorophenolics, Tet-CC and TCS were not detected after treatment. 2,6-DCSA was removed up to 93% and 5,6-DCV up to 68%. Tet-CP were not detected in the effluent after photocatalysis. TCP were removed up to 83% followed by MCP (61%) and DCP (40%) (Figure 4.14 d).

4.3.3.7 cRFA removal

Higher cRFA removal efficiency was observed for ODED sequence effluents, i.e. 35 and 38% for D_1 stage and 15 and 18% for E stage effluents, followed by DE_PD, DED, and D/CED sequences (Table 4.9). This is due to the low initial color and organic load of ODED sequence effluents as compared to effluents of other bleaching sequences. The lower cRFA removal efficiency was observed for E or E_P stage effluents as compared to D/C or D_1 stages effluents. The E or E_P stage effluents were having higher amount of color as compared to D/C or D_1 stage effluents. Hence lower efficiency. Low effluent color allows efficient penetration of UV radiation into the reaction mixture. cRFA were removed to lower extent as compared to chlorophenolic compounds after photocatalytic treatment. This may be due to the higher concentration of cRFA present in the effluents as compared to chlorophenolics.

(a) cRFA removal for D/CED sequence effluents

$UV/TiO_2/H_2O_2$ process was found more effective for the removal of cRFA as compared to UV/TiO_2 process. For D/C stage effluent, 9,10,12,13-tetrachlorostearic acid (TCSA) was removed to the highest extent, i.e. 65 and 74%, followed by 12,14-dichlorodehydroabietic acid (DCDAA), 20 and 25%, and chlorodehydroabietic acid (CDAA), 12 and 15%, after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. Lower cRFA removal efficiency was observed in case of E stage as compared to D/C stage effluent of D/CED sequence. TCSA and DCDAA were removed up to 16 and 8%, respectively, after treatment by $UV/TiO_2/H_2O_2$ process which is higher as compared to UV/TiO_2 process. CDAA was removed up to 2% after treatment by both the processes (Table 4.9). Chloro-fatty acids (cFA) were removed to the highest extent as compared to chloro-resin acids (cRA). For D/C stage, cFA were removed up to 65 and 74% while cRA were removed up to 15 and 19% after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. For E stage effluent, cFA were removed up to 12 and 16% after treatment with UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. While, cRA were removed up to 4% after treatment by both the processes (Table 4.10).

(b) cRFA removal for DED sequence effluents

For D_1 stage effluent of DED sequence, TCSA was removed up to 45 and 52%, DCDAA 47 and 49%, and CDAA 13 and 19%, after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. cRFA were removed to lower extent in case of E stage effluent. TCSA was removed to the maximum extent, i.e. 36 and 42%, followed by DCDAA, 9 and 12%, and CDAA, 6 and 7%, after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively (Table 4.9). cFA were removed to the highest extent as compared to cRA. For D_1 stage, cFA were removed up to 45 and 52% while cRA were removed up to 22 and 26% after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. In case of E stage effluent, cFA were removed up to 36 and 42% while cRA were removed up to 7 and 9% after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively (Table 4.10).

(c) cRFA removal for DE_PD sequence effluents

For D_1 stage effluent, DCDAA was removed to the highest extent, 54 and 63%, followed by TCSA, 53 and 60%, and CDAA, 17 and 23%, after treatment by UV/TiO_2 and

$UV/TiO_2/H_2O_2$ processes, respectively. Lower cRFA removal efficiency was observed in case of E_P stage effluent. Out of the two cRFA identified in E_P stage effluent, DCDAA was removed up to 11 and 16%, and CDAA 7 and 9%, after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively (Table 4.9). cFA were removed to the highest extent as compared to cRA. For D_1 stage, cFA were removed up to 53 and 60% while cRA were removed up to 26 and 33% after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. In E_P stage effluent, only cRA were detected which were removed up to 9 and 12% after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively (Table 4.10).

(d) cRFA removal for ODED sequence effluents

TCSA was not detected in ODED sequence effluents. For D_1 stage, DCDAA was removed up to 63 and 68%, and CDAA 24 and 27% after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively (Table 4.9). cRFA were removed to higher extent in case of D_1 stage as compared to E stage. For E stage, DCDAA was removed up to 20 and 24%, and CDAA 12 and 15%, after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. cFA were not detected in ODED sequence effluents. cRA were removed up to 35 and 38% for D_1 stage and 15 and 39% for E stage effluents after treatment by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively (Table 4.10).

Photocatalytic treatment was able to degrade chlorophenolics and cRFA. $UV/TiO_2/H_2O_2$ process was having higher efficiency as compared to UV/TiO_2 process. The highly substituted phenolics were removed to the significant extent. While, the lower efficiency was observed in case of cRFA, which may be due to the low lamp power and their high concentration as compared to chlorophenolics.

4.3.4 Paper mill effluents treatment

4.3.4.1 Characteristics of effluents

The average analytical characteristics of PC and biotreated (BT) paper mill (Mill-A and Mill-B) effluents utilized for the present study are summarized in Table 4.11-4.13. Mill-A effluents were characterized with higher pollution load in terms of BOD, COD, and color, as compared to Mill-B. PC effluents of both Mills presented high organic load as compared to BT effluents. Mill-B effluents were having higher amount of AOX and chlorophenolics as compared to Mill-A. BOD/COD ratio of the effluents was low, i.e. 0.25 and 0.12 for PC and BT effluents of Mill-A and 0.34 and 0.12 for PC and BT effluents of Mill-B, indicating low biodegradability of the organics present in the effluents (Table 4.11). Four cRFA, i.e. CDAA, DCDAA, 9,10-dichlorostearic acid (DCSA), and TCSA were detected in the paper mill effluents (Table 4.12). Higher concentration of cRFA was detected in Mill A effluents than Mill B effluents. PC effluents of both the Mills were having higher concentration of cRFA as compared to BT effluents.

For Mill A, GC/MS analysis facilitated identification of 19 and 17 low molecular weight (LMW) chlorophenolic compounds in PC and BT effluents, respectively (Table 4.13). Similar compounds have also been reported to be present in paper mill effluents by other authors [20, 43]. Among the identified chlorophenolics, CP (82% in PC and 69% in BT) and CG (16% in PC and 30% in BT) were the major components. CC and CV were not detected in BT effluent. CS, CV, CSA, and CC in PC effluent and CSA and CS in BT effluent were detected in trace quantities (<1%) (Figure 4.15 a and c). For PC effluent, the highest contribution came from TCP (40%) followed by DCP (36%) and MCP (24%). While, for BT effluent, DCP were the major contributors (50%) followed by TCP (29%) and MCP (21%). These results indicate that 76 and 79% of the identified compounds in PC and BT effluents, respectively, were DCP and TCP (Figure 4.15 b and d). These findings are in good agreement with the literature [44]. In PC effluent, 3,4,5-TCG and Tet-CG were not detected. 2,3,6-TCP, 3,6-DCC, 4,5,6-TCG, and 5,6-DCV were identified only in PC effluent. Degradation of these compounds, complete or below detectable amount, during the biological treatment may be the possible reason. In case of BT effluent, 3,4,5-TCG, 4,5,6-TCG, and Tet-CG were not detected. 2,3-DCP and 2,3,5-TCP were identified only in BT effluent. This may be due to the possible dilution of these compounds below detectable concentration in the influent of primary clarifier. The quantities of 2,5-DCP, 4,6-DCG, and 3,4,6-TCG were higher in BT effluent as compared to PC effluent. This may be due to the possible transformation of one compound into another during biological treatment or concentration because of treatment system residence time [45]. PCP was not detected in both the effluents (Table 4.13).

In case of Mill-B, 24 and 18 chlorophenolic compounds were identified in PC and BT effluents, respectively (Table 4.13). For PC effluent, the major contribution came from CP

(31%) followed by CG and CC (25%), CS (12%), and CSA (7%) (Figure 4.15 e). While in case of BT effluent, major contribution came from CC (37%) followed by CP (23%), CS (17%), CG (12%), and CSA (11%) (Figure 4.15 g). CV was present in minor quantity in PC effluent (0.4%) while not detected in BT effluent. For PC effluent, the highest contribution came from DCP (57%) followed by TCP (32%), Tet-CP (8%), and MCP (3%). PCP was not detected (Figure 4.15 f). While, for BT effluent, DCP (55%) were the major contributors followed by TCP (35%) and Tet-CP (9%). PCP and MCP were detected in small quantity (<1%) (Figure 4.15 h). 89 and 90% of the identified compounds in PC and BT effluents, respectively, were DCP and TCP. 3-CP, 3,4-DCP, 4-CG, 2,3,6-TCP, 2,3,4-TCP, 3,5-DCC, and 5,6-DCV were identified only in PC effluent. In case of BT effluent, 4-CG was not detected. While, 2,3-DCP was not detected in both the effluents (Table 4.13).

In PC effluent of Mill A, among cRFA major contribution came from DCSA (41%) followed by CDAA (24%), TCSA (21%), and DCDAA (14%) (Figure 4.16 a). While in case of PC effluent of Mill B, TCSA (48%) was the predominant component followed by DCDAA (23%), DCSA (22%), and CDAA (7%) (Figure 4.16 e). DCSA (40%) is the major component of BT effluent of Mill A followed by TCSA (33%) and CDAA (27%) (Figure 4.16 b). For BT effluent of Mill B, major contribution came from TCSA (81%) followed by CDAA (16%) and DCDAA (3%) (Figure 4.16 f). cFA were present in higher amount as compared to cRA. cFA contributed to 62 and 74% while cRA to 38 and 26% for PC and BT effluents of Mill A, respectively (Figure 4.16 c and d). While in case of Mill B, 69 and 81% contribution came from cFA and 31 and 19% from cRA for PC and BT effluents, respectively (Figure 4.16 g and h).

The presence of chloroorganics in BT effluent proves the low efficiency of the microbial processes for the degradation of these compounds. Hence, the advanced photocatalytic oxidation of PC and BT paper mill effluents have been investigated using UV/TiO_2, Solar/TiO_2, UV/TiO_2/H_2O_2, and Solar/TiO_2/H_2O_2 processes. PC effluents of both Mill were diluted to bring the initial COD load to 500 mg/L before photocatalytic oxidation while BT effluents were used directly.

4.3.4.2 COD removal

COD, an important measure of water pollution, is necessary to be monitored during the photocatalytic degradation of effluent. UV/TiO_2/H_2O_2 process resulted in 58 and 75% removal of COD followed by Solar/TiO_2/H_2O_2, 52 and 70%, UV/TiO_2, 47 and 65%, and Solar/TiO_2, 45 and 59%, processes for PC and BT effluents of Mill A, respectively (Figure 4.17 a). For Mill B, UV/TiO_2/H_2O_2 process resulted in 58 and 80% removal of COD followed by Solar/TiO_2/H_2O_2, 53 and 75%, UV/TiO_2, 52 and 77%, and Solar/TiO_2, 48 and 70%, processes for PC and BT effluents, respectively (Figure 4.19 a). Higher COD removal efficiency was observed for Mill B effluents as compared to Mill A effluents. The Mill A effluents were having higher color as compared to Mill B effluents. The color may reduce the photodegradation efficiency by inhibiting penetration of light radiation to the catalyst surface. Higher COD removal efficiency was achieved for BT effluents as compared to PC effluents. Balcioglu and Arslan [46] also reported higher COD removal in case of BT effluents. Biotreatment converts some of the functional groups of organic pollutants to more easily oxidisable forms that are then easily degraded by photocatalysis. The difference in COD removal efficiency for effluents of Mill A and B may be due to the difference in the molecular weight and structure of the dissolved pollutants originating from different bleaching processes [46]. Peralta-Zamora et al. [47] reported 80% COD removal from 250 mL paper mill effluent after 2 h of treatment using TiO_2 (predominantly anatase, 30 m^2/g) under irradiation by a 125 W lamp. COD removal in our case remained in range of 52-58% for PC effluents by UV/TiO_2/H_2O_2 and Solar/TiO_2/H_2O_2 processes. Lower COD removal achieved may be due to the low power of UV and solar radiation and higher reaction volume (500 mL).

4.3.4.3 BOD removal

UV/TiO_2/H_2O_2 process resulted in 43 and 53% removal of BOD followed by Solar/TiO_2/H_2O_2, 38 and 49%, UV/TiO_2, 34 and 37%, and Solar/TiO_2, 32 and 35%, processes for PC and BT effluents of Mill A, respectively (Figure 4.17 b). For Mill B, UV/TiO_2/H_2O_2 process resulted in 39 and 55% removal of BOD followed by Solar/TiO_2/H_2O_2, 35 and 49%, UV/TiO_2, 31 and 51%, and Solar/TiO_2, 30 and 45%, processes for PC and BT effluents, respectively (Figure 4.19 b). Higher BOD removal was achieved for PC effluent of Mill A and BT effluent of Mill B as compared to PC effluent of Mill B and BT effluent of Mill A, respectively. BOD/COD ratio improved to 0.34, 0.33, 0.31, and 0.31 for PC effluent and 0.22, 0.21, 0.21, and 0.19 for BT effluent of Mill A after photocatalytic treatment by UV/TiO_2/H_2O_2, Solar/TiO_2/H_2O_2, UV/TiO_2, and Solar/TiO_2 processes, respectively (Figure 4.17 c). While in case of Mill B, BOD/COD ratio improved to 0.49, 0.46, 0.48, and 0.45 for PC effluent and 0.27, 0.24, 0.25, and 0.22 for BT effluent after treatment by UV/TiO_2/H_2O_2, Solar/TiO_2/H_2O_2, UV/TiO_2, and Solar/TiO_2 processes, respectively. For PC effluent of Mill B, BOD/COD ratio improved above the optimal value (0.4) (Figure 4.19 c). These findings indicate easy removal of pollutants in biological treatment plant. Balcioglu and Arslan [46] also observed improvement in BOD/COD ratio after photocatalysis after 5 h of treatment. Yeber et al. [38] reported rapid COD removal and slight improvement in BOD/COD ratio of the effluents after photocatalysis. Yeber et al. [42, 48] stated that photocatalysis could be a good pre-oxidation step to the biological treatment as the biodegradability of the residual organic matter is improved. The partial mineralisation and structural changes in the organic pollutants are the fundamental for BOD/COD ratio improvement and toxicity reduction of the effluents and chlorinated phenols [48].

4.3.4.4 Color removal

The photocatalytic treatment was found to be highly efficient for the discoloration of paper mill effluents. Solar/TiO_2/H_2O_2 process resulted in 96 and 99% removal of color followed by UV/TiO_2/H_2O_2, 89 and 95%, Solar/TiO_2, 83 and 88%, and UV/TiO_2, 75 and 79%, processes for PC and BT effluents of Mill A, respectively (Figure 4.18 a). For Mill B, Solar/TiO_2/H_2O_2 process resulted in 95 and 98% removal of color followed by UV/TiO_2/H_2O_2, 93 and 98%, Solar/TiO_2, 87 and 95%, and UV/TiO_2, 85 and 95%, processes for PC and BT effluents of Mill B, respectively (Figure 4.20 a). Higher color removal efficiency was achieved in case of BT effluents compared to PC effluents. BT effluents were having lower organic load and color as compared to PC effluents hence higher discoloration was observed. Balcioglu and Arslan [46] also observed higher color removal efficiency for pretreated effluents after photocatalysis. Balcioglu and Cecen [19] reported almost complete color removal after 1 h of treatment with UV/TiO_2/H_2O_2 using 15 mM/L of H_2O_2. Our results are supported by the above statement as we also obtained significant color removal after photocatalysis. Yeber et al. [48] stated that the effluent discoloration occurs by degradation of phenolic lignin like material and high molecular mass compounds, which are responsible for color.

4.3.4.5 AOX removal

$UV/TiO_2/H_2O_2$ process resulted in 57 and 62% removal of AOX followed by $Solar/TiO_2/H_2O_2$, 55 and 59%, UV/TiO_2, 49 and 55%, and $Solar/TiO_2$, 45 and 51%, processes for PC and BT effluents of Mill A, respectively (Figure 4.18 b). For Mill B, $UV/TiO_2/H_2O_2$ process resulted in 24 and 28% removal of AOX followed by $Solar/TiO_2/H_2O_2$, 18 and 26%, UV/TiO_2, 17 and 23%, and $Solar/TiO_2$, 15 and 19%, processes for PC and BT effluents, respectively (Figure 4.20 b).The Mill B effluents were having higher concentration of AOX as compared to Mill A effluents hence lower removal efficiency was observed. Yeber et al. [42] reported 85 and 95% AOX removal within 60 and 120 min, respectively, of photocatalytic treatment using immobilized catalyst. The high removal in a short period was reported to be due to high irradiation power of lamp as compared to the sunlight. In our case the low removal efficiency may be due to low power of UV lamp used. We also obtained higher removal with UV lamps as compared with the sunlight. The reduction in effluents toxicity in terms of removal of AOX and improvement in biodegradability of the effluents are the significant results. These observations are in good agreement with the literature [18, 48].

4.3.4.6 Chlorophenolics removal

(a) Chlorophenolics removal for Mill A effluents

For PC effluent of Mill A, 68% removal of chlorophenolics was achieved by $UV/TiO_2/H_2O_2$ process followed by $Solar/TiO_2/H_2O_2$ (61%), UV/TiO_2 (59%), and $Solar/TiO_2$ (52%) processes (Table 4.14). $UV/TiO_2/H_2O_2$ process removed CV and CS below detection after treatment. CSA were removed up to 84% followed by CC (81%), CG (79%), and CP (65%) (Figure 4.21 a). Chlorophenolics were removed in the range of 53-100%. Among CP, 2,5-DCP and 2,3,4-TCP were not detected after photocatalytic oxidation. 2,3,6-TCP was removed up to the maximum extent (91%) followed by 4-CP and 3,4-DCP (86%), 3-CP (73%), and 2,4,6-TCP (70%). Remaining CP were removed up to 64%. 4,5,6-TCG was completely removed by photocatalysis. 4,6-DCG was removed up to 88% followed by 4,5-DCG (82%), 4-CG (74%), and 3,4,6-TCG (66%). Among other chlorophenolics, 5,6-DCV and TCS were not detected after photocatalysis. 2,6-DCSA and 3,6-DCC were removed up to 84 and 81%, respectively (Table

4.14). MCP were removed up to the highest extent (76%) followed by DCP (75%) and TCP (56%) (Figure 4.21 c).

UV/TiO_2 process removed CS below detection after treatment. CV was removed up to 82% followed by CC (72%), CSA (71%), CG (65%), and CP (57%) (Figure 4.21 a). Chlorophenolics were removed in the range of 48-100%. Among CP, 2,5-DCP was removed up to the highest extent (76%) followed by 3,4-DCP (75%), 4-CP (74%), and 2,3,4-TCP (67%). The remaining CP were removed in the range of 48-65%. 4,5,6-TCG was not detected after the photocatalytic oxidation. 4,6-DCG was removed up to 69% followed by 4-CG (68%), 4,5-DCG (67%), and 3,4,6-TCG (51%). TCS was not detected after photocatalytic treatment. 5,6-DCV was removed up to 82% followed by 3,6-DCC (72%) and 2,6-DCSA (71%) (Table 4.14). MCP were removed up to the maximum extent, i.e. 68%, followed by DCP (63%) and TCP (50%) (Figure 4.21 c).

Solar/TiO_2/H_2O_2 process removed CC, CV, CS, and CSA below detection after treatment. CG and CP were removed up to the extent of 72 and 58%, respectively (Figure 4.21 b). Chlorophenolics were removed in the range of 44-100%. 2,3,6-TCP was not detected after photocatalytic oxidation. 2,5-DCP was removed up to the extent of 97% followed by 2,3,4-TCP (94%), 3,4-DCP (85%), and 4-CP (74%). Remaining CP were removed in the range of 44-68%. 4,5,6-TCG was completely oxidized by photocatalysis. 4,5-DCG was removed up to 78% followed by 4-CG (71%), 3,4,6-TCG (70%), and 4,6-DCG (60%). Other chlorophenolics i.e. 3,6-DCC, 5,6-DCV, TCS, and 2,6-DCSA were not detected after photocatalysis (Table 4.14). MCP were removed to the highest extent, i.e. 69%, followed by DCP (66%) and TCP (53%) (Figure 4.21 d).

Solar/TiO_2 process removed CC, CV, and CS below detection after treatment. CG were removed up to 62% followed by CP (50%) and CSA (39%) (Figure 4.21 b). Chlorophenolics were removed in the range of 34-100%. 3,4-DCP was removed up to the maximum extent, i.e. 87%, followed by 2,3,4-TCP (83%) and 2,5-DCP (72%). Remaining CP were removed in the range of 36-52%. 4,5,6-TCG was not detected after photocatalysis. 4,6-DCG was removed up to 88% followed by 3,4,6-TCG (65%), 4,5-DCG (64%), and 4-CG (34%). Among remaining chlorophenolics, 3,6-DCC, 5,6-DCV, and TCS were not detected after treatment. 2,6-DCSA was removed up to 39% (Table 4.14). DCP were removed to the highest extent (61%) followed by MCP (48%), and TCP (47%) (Figure 4.21 d).

For BT effluent, 75% removal of chlorophenolics was achieved by UV/TiO_2/H_2O_2 process followed by Solar/TiO_2/H_2O_2 (73%), UV/TiO_2 (68%), and Solar/TiO_2 (66%) processes (Table 4.15). UV/TiO_2 and UV/TiO_2/H_2O_2 processes removed CS and CSA below detection after treatment. UV/TiO_2/H_2O_2 process removed CP and CG up to 75 and 74%, respectively (Figure 4.22 a). Chlorophenolics were removed in the range of 65-100%. 2,3-DCP, 2,3,5-TCP, and 2,4,6-TCP were not detected in the effluent after photocatalysis. 4-CP was removed up to the maximum extent (91%) followed by 2,3,4-TCP (87%), 2,6-DCP (85%), and 2,5-DCP (79%). The remaining CP were removed in the range of 65-78%. 4-CG and 4,6-DCG were removed up to the highest extent (76%) followed by 3,4,6-TCG (75%) and 4,5-DCG (68%). Among remaining chlorophenolics, TCS and 2,6-DCSA were not detected in the photocatalysed effluent (Table 4.15). MCP were removed to the highest extent (81%) followed by DCP (77%) and TCP (69%) (Figure 4.22 c).

UV/TiO_2 process removed CP and CG up to 68 and 69%, respectively (Figure 4.22 a). Chlorophenolics were removed in the range of 58-100%. 2,3,5-TCP was not detected after photocatalytic treatment. 4-CP was removed up to 86%, followed by 2,3-DCP (80%), 2,5-DCP (76%), 3-CP and 3,4-DCP (75%). The remaining CP were removed in the range of 58-71%. Among CG, 4,6-DCG was removed up to the highest extent (74%) followed by 4-CG (69%), 3,4,6-TCG (67%), and 4,5-DCG (65%). TCS and 2,6-DCSA were not detected in the effluent after photocatalysis (Table 4.15). MCP were removed to the highest extent (76%) followed by DCP (70%) and TCP (61%) (Figure 4.22 c).

Solar/TiO_2/H_2O_2 process removed CS and CSA below detection after treatment. CG and CP were removed up to 74 and 72%, respectively (Figure 4.22 b). Chlorophenolics were removed in the range of 62-100%. 2,3-DCP, 2,3,5-TCP, and 2,4,6-TCP were not detected in the effluent after photocatalytic treatment. 2,3,4-TCP was removed up to the extent of 93%, followed by 4-CP (92%), 2,6-DCP (82%), and 3,4-DCP (81%). The remaining CP were removed in the range of 62-74%. 4,6-DCG was removed up to the highest extent (88%) followed by 3,4,6-TCG (71%), 4,5-DCG (68%), and 4-CG (64%). Among remaining chlorophenolics, TCS and 2,6-DCSA were not detected in the photocatalysed effluent (Table

4.15). DCP were removed to the highest extent (78%) followed by MCP (72%) and TCP (66%) (Figure 4.22 d).

Solar/TiO_2 process removed CS below detection after treatment. CG and CSA were removed by 75% and CP by 61% (Figure 4.22 b). Chlorophenolics were removed in the range of 50-100%. 2,3-DCP and 2,3,5-TCP were not detected in the effluent after photocatalytic treatment. 2,4,6-TCP was removed up to the extent of 86%, followed by 2,5-DCP (80%), 3,4-DCP (75%), 4-CP (72%), and 3-CP (71%). The remaining CP were removed in the range of 50-67%. 4,5-DCG was removed up to the highest extent (81%) followed by 3,4,6-TCG (79%), 4,6-DCG (78%), and 4-CG (59%). TCS was not detected and 2,6-DCSA was removed up to 75% (Table 4.15). DCP were removed to the highest extent (70%) followed by MCP (68%) and TCP (58%) (Figure 4.22 d).

(b) Chlorophenolics removal for Mill B effluents

For PC effluent, 43% removal of chlorophenolics was achieved by UV/TiO_2/H_2O_2 process followed by Solar/TiO_2/H_2O_2 (39%), UV/TiO_2 (37%), and Solar/TiO_2 (34%) processes (Table 4.16). UV/TiO_2/H_2O_2 process removed CV to the highest extent (79%) followed by CSA and CG (56%), CP (43%), CS (36%), and CC (29%) (Figure 4.23 a). Chlorophenolics were removed in the range of 15-100%. 3,4-DCP and 2,4,6-TCP were not detected after photocatalytic oxidation. 3-CP was removed up to 86% followed by 2,3,4-TCP (86%), 4-CP (84%), and 2,3,5-TCP (81%). Remaining CP were removed in the range of 34-67%. 4,5-DCG was removed to the highest extent (78%) followed by 4,5,6-TCG (77%), 4-CG (68%), and 3,4,5-TCG (67%). Remaining CG were removed in the range of 42-63%. Tet-CC was removed up to the highest extent (74%) followed by 3,5-DCC (67%), and 3,6-DCC (15%). 5,6-DCV, 2,6-DCSA, and TCS were removed up to 79, 56, and 36%, respectively (Table 4.16). MCP were removed to the highest extent (80%) followed by Tet-CP (67%), TCP (43%), and DCP (38%) (Figure 4.23 c).

UV/TiO_2 process removed CV to the highest extent (67%) followed by CSA (49%), CG (48%), CP (38%), CS (32%), and CC (24%) (Figure 4.23 a). Chlorophenolics were removed in the range of 12-88%. 2,4,6-TCP was removed to the highest extent (88%) followed by 3,4-DCP (85%), 4-CP (81%), 3-CP (80%), and 2,3,5-TCP (74%). The remaining CP were removed in the range of 29-69%. 4,5-DCG was removed to the maximum extent (70%) followed by 4-CG

(63%), 4,5,6-TCG (62%), and 3,4,5-TCG (60%). Other CG were removed in the range of 34-58%. Tet-CC was removed up to the highest extent (65%) followed by 3,5-DCC (62%) and 3,6-DCC (12%). 5,6-DCV was removed up to the extent of 67% followed by 2,6-DCSA (49%) and TCS (32%) (Table 4.16). MCP were removed to the highest extent (75%) followed by Tet-CP (60%), TCP (36%), and DCP (32%) (Figure 4.23 c).

Solar/TiO_2/H_2O_2 process removed CV to the highest extent (71%) followed by CSA and CG (50%), CP (39%), CS (35%), and CC (26%) (Figure 4.23 b). Chlorophenolics were removed in the range of 14-100%. 3,4-DCP, 2,3,6-TCP, and 2,4,6-TCP were not detected after photocatalytic oxidation. 2,3,4-TCP was removed up to 85% followed by 4-CP (82%), 3-CP (77%), 2,3,5-TCP (75%), and 2,6-DCP (70%). Remaining CP were removed in the range of 30-43%. 4,5-DCG was removed to the highest extent (70%) followed by 4-CG (65%), 3,4,5-TCG (62%), and 4,5,6-TCG (59%). Remaining CG were removed in the range of 37-57%. Tet-CC was removed up to the highest extent (66%) followed by 3,5-DCC (57%) and 3,6-DCC (14%). 5,6-DCV, 2,6-DCSA, and TCS were removed up to 71, 50, and 35%, respectively (Table 4.16). MCP were removed to the highest extent (74%) followed by Tet-CP (60%), TCP (39%), and DCP (34%) (Figure 4.23 d).

Solar/TiO_2 process resulted in highest removal of CV (63%) followed by CSA (46%), CG (45%), CP (35%), CS (29%), and CC (20%) (Figure 4.23 b). Chlorophenolics were removed in the range of 10-94%. 3,4-DCP was removed to the highest extent (94%) followed by 2,4,6-TCP (90%), 4-CP (75%), 3-CP (74%), 2,3,6-TCP and 2,3,4-TCP (71%). The remaining CP were removed in the range of 27-68%. 4,5-DCG was removed to the maximum extent (66%) followed by 4-CG (59%), 3,4,6-TCG, 3,4,5-TCG, and 4,5,6-TCG (53%), Tet-CG (50%), and 4,6-DCG (33%). Tet-CC was removed up to the highest extent (58%) followed by 3,5-DCC (51%) and 3,6-DCC (10%). 5,6-DCV was removed up to the extent of 63% followed by 2,6-DCSA (46%) and TCS (29%) (Table 4.16). MCP were removed to the highest extent (69%) followed by Tet-CP (53%), TCP (34%), and DCP (30%) (Figure 4.23 d).

For BT effluent of Mill B, 61% removal of chlorophenolics was achieved by UV/TiO_2/H_2O_2 process followed by Solar/TiO_2/H_2O_2 and UV/TiO_2 (55%), and Solar/TiO_2 (49%) processes (Table 4.17). UV/TiO_2/H_2O_2 process resulted in the highest removal of CG (84%) followed by CP (80%), CSA (67%), CS (61%), and CC (41%) (Figure 4.24 a).

Chlorophenolics were removed in the range of 37-100%. 4-CP, 2,6-DCP, 2,4-DCP, 2,3,5-TCP, 2,4,6-TCP, and PCP were not detected after photocatalytic oxidation. 2,5-DCP and 2,4,5-TCP were removed up to 88 and 71%, respectively. 4,6-DCG and 4,5,6-TCG were not detected after treatment. 4,5-DCG and 3,4,5-TCG were removed up to 97% followed by 3,4,6-TCG (96%) and Tet-CG (68%). Tet-CC and 3,6-DCC were removed up to 86 and 37%, respectively. 2,6-DCSA and TCS were removed up to 67 and 61%, respectively (Table 4.17). MCP and PCP were not detected after photocatalysis. Tet-CP were removed up to 75% followed by TCP (70%) and DCP (53%) (Figure 4.24 c).

UV/TiO_2 process resulted in the highest removal of CG (77%) followed by CP (72%), CSA (60%), CS (54%), and CC (36%) (Figure 4.24 a). Chlorophenolics were removed in the range of 33-100%. 4-CP, 2,6-DCP, and 2,4,6-TCP were not detected after photocatalytic oxidation. 2,4-DCP was removed up to 85% followed by 2,3,5-TCP (84%), 2,5-DCP (79%), PCP (71%), and 2,4,5-TCP (65%). 4,6-DCG was removed to the maximum extent (94%) followed by 3,4,6-TCG (93%), 4,5,6-TCG (88%), 4,5-DCG (86%), 3,4,5-TCG (85%), and Tet-CG (62%). Tet-CC and 3,6-DCC were removed up to 71 and 33%, respectively. 2,6-DCSA and TCS were removed up to 60 and 54%, respectively (Table 4.17). MCP were not detected after photocatalysis. PCP was removed up to 71% followed by Tet-CP (65%), TCP (63%), and DCP (48%) (Figure 4.24 c).

Solar/TiO_2/H_2O_2 process removed CG to the highest extent (80%) followed by CP (70%), CSA (58%), CS (55%), and CC (36%) (Figure 4.24 b). Chlorophenolics were removed in the range of 32-100%. 4-CP, 2,6-DCP, 2,3,5-TCP, 2,4,6-TCP, and PCP were not detected after photocatalytic oxidation. 2,4-DCP was removed up to 97% followed by 2,5-DCP (74%) and 2,4,5-TCP (60%). 3,4,6-TCG was not detected after photocatalysis. 4,5,6-TCG was removed up to 94% followed by 4,5-DCG (93%), 4,6-DCG (90%), 3,4,5-TCG (88%), and Tet-CG (63%). Tet-CC and 3,6-DCC were removed up to 76 and 32%, respectively. 2,6-DCSA and TCS were removed up to 58 and 55%, respectively (Table 4.17). MCP and PCP were not detected after treatment. Tet-CP was removed up to 68% followed by TCP (62%) and DCP (47%) (Figure 4.24 d).

Solar/TiO_2 process resulted in the highest removal of CG (72%) followed by CP (65%), CSA (52%), CS (49%), and CC (33%) (Figure 4.24 b). Chlorophenolics were removed in the range of 30-100%. 4-CP, 2,6-DCP, and 2,4,6-TCP were not detected after photocatalytic oxidation. PCP was removed up to 88% followed by 2,3,5-TCP (86%), 2,4-DCP (80%), 2,5-DCP (69%), and 2,4,5-TCP (56%). 4,6-DCG and 4,5,6-TCG were removed to the maximum extent (87%) followed by 3,4,6-TCG and 3,4,5-TCG (86%), 4,5-DCG (82%), and Tet-CG (56%). Tet-CC and 3,6-DCC were removed up to 63 and 30%, respectively. 2,6-DCSA and TCS were removed up to 52 and 49%, respectively (Table 4.17). MCP were not detected after treatment. PCP was removed up to 88% followed by Tet-CP (59%), TCP (57%), and DCP (43%) (Figure 4.24 d).

4.3.4.7 cRFA removal

(a) cRFA removal for Mill A effluents

For Mill A, 40-48% and 29-35% cRFA removal was achieved for PC and BT effluents, respectively, after treatment by different processes. For PC effluent, DCDAA was removed in the range of 51-68% followed by CDAA (46-53%), TCSA (39-48%), and DCSA (32-38%) after treatment by different processes. Comparatively higher cRFA removal efficiency was observed by $UV/TiO_2/H_2O_2$ process followed by UV/TiO_2, $Solar/TiO_2/H_2O_2$, and $Solar/TiO_2$ processes. For DCSA, higher removal was achieved with $UV/TiO_2/H_2O_2$ process followed by $Solar/TiO_2/H_2O_2$, UV/TiO_2, and $Solar/TiO_2$ processes (Table 4.18). cRA were removed to the higher extent (48-59%) as compared to cFA (35-41%) (Figures 4.25 a and b). For BT effluent, CDAA was removed in the range of 36-41% followed by TCSA (28-36%), and DCSA (26-32%) after treatment by different processes. Comparatively higher performance was achieved by $UV/TiO_2/H_2O_2$ process followed by $Solar/TiO_2/H_2O_2$, UV/TiO_2, and $Solar/TiO_2$ processes (Table 4.18). cRA were removed to the higher extent (36-41%) compared to cFA (27-34%) (Figures 4.25 c and d).

(b) cRFA removal for Mill B effluents

While in case of Mill B, cRFA were removed in the range of 26-34% and 43-51% for PC and BT effluents, respectively. For PC effluent, CDAA was removed to the highest extent (61-68%) followed by DCDAA (37-45%), DCSA (34-41%), and TCSA (12-21%) after treatment by different processes. Comparatively higher performance was achieved by $UV/TiO_2/H_2O_2$ process followed by UV/TiO_2, $Solar/TiO_2/H_2O_2$, and $Solar/TiO_2$ processes

(Tables 4.19). cRA were removed to the higher extent (43-50%) as compared to cFA (19-27%) (Figures 4.25 e and f). While for BT effluent, DCDAA was removed to the highest extent (90-100%) followed by CDAA (78-85%), and TCSA (34-43%) after treatment by different processes. For CDAA, higher removal was achieved by UV/TiO_2/H_2O_2 process followed by UV/TiO_2, Solar/TiO_2/H_2O_2, and Solar/TiO_2 processes. While for TCSA, higher removal was achieved with UV/TiO_2/H_2O_2 process followed by Solar/TiO_2/H_2O_2, UV/TiO_2, and Solar/TiO_2 processes. DCDAA was not detected after treatment by UV/TiO_2/H_2O_2, Solar/TiO_2/H_2O_2, and Solar/TiO_2 processes (Tables 4.19). cRA were removed to the higher extent (81-87%) as compared to cFA (34-42%) (Figures 4.25 g and h).

Higher pollutants removal efficiency was achieved with UV/TiO_2/H_2O_2 and Solar/TiO_2/H_2O_2 processes as compared to UV/TiO_2 and Solar/TiO_2 processes. Machado et al. [21] reported 20-30% increase in reaction rate by the addition of H_2O_2. H_2O_2 can produce additional $OH^\bullet$ radicals by its decomposition and reaction with superoxide radical. It can also accept conduction band e^- thus prevent e^-/h^+ re-combination. The $OH^\bullet$ radicals can be produced easily from H_2O_2 splitting as compared to H_2O [49]. The photocatalytic oxidation of a variety of organic pollutants occurs by the concomitant action of highly reactive intermediates, i.e. hydroxyl radicals ($OH^\bullet$), holes (h^+), superoxide radicals ($O_{2ads}^{\bullet-}$), and hydroperoxyl radicals ($OOH^\bullet$) [50]. The rate and efficiency of the photodegradation of phenol and its derivatives depends on the catalyst concentration, light intensity, solution pH, pollutant (phenol and its derivatives) concentration, and the presence of electron acceptor [51]. Peiro et al. [52] reported photocatalytic degradation of phenol and orthosubstituted phenolic compounds to be: guaiacol > 2-CP = phenol > CC. Higher pollutants removal efficiency was achieved for BT effluents as compared to PC. The biological treatment may convert some functional groups of organic pollutants to more easily oxidisable forms that are then easily degraded during photocatalysis [46]. The chloroorganics present in pulp bleaching and paper mill effluents were removed to different extent after treatment by photocatalysis. The possible reason behind this may be the different processes used for pulp bleaching, initial concentration, and presence of reaction intermediates which compete for photoactive sites. Parida and Parija [53] examined the effect of initial substrate concentration on the photocatalytic degradation of phenol. The degradation efficiency decreased from 100 to 60% as the substrate concentration increased under solar irradiation. While under UV light, the degradation was decreased from 94 to 52% with increase in initial concentration.

Tanaka and Saha [54] reported that 2,4,6-trichlorophenol (2,4,6-TCP) adsorption onto TiO_2 surface does not play any significant role in the degradation. The $OH^•$ radicals generation is a key factor which finally mineralizes 2,4,6-TCP to HCl and CO_2. Huang et al. [55] reported that photocatalytic oxidation of aromatic compounds depends on the substituent group and MCP degrade faster than DCP or TCP. Ilyas et al. [28] reported that the degradation rate of CP decreases as the number of chlorine atoms on the phenolic ring increase. The photo transformation rate of 2,4-DCP and 2,5-DCP was high as compared to 2,4,6-TCP. The sites on the aromatic ring, which are not occupied by chlorine atoms are generally attacked by $OH^•$ radicals. So, higher no of chlorine atoms on the aromatic ring decreases the reactivity towards $OH^•$ radicals [56]. Huang et al. [55] reported that photocatalytic (UV/TiO_2) degradation of MCP follows the order 4-CP = 3-CP = 2-CP, for DCP, 2,3-DCP > 3,5-DCP = 2,5-DCP > 3,4-DCP > 2,4-DCP > 2,6-DCP, and for TCP, 3,4,5-TCP = 2,3,5-TCP > 2,3,4-TCP = 2,4,5-TCP = 2,3,6-TCP > 2,4,6-DCP. While by $UV/TiO_2/H_2O_2$ process, the rate of degradation of chlorophenols is fast and follows the order: 4-CP > 3-CP > 2-CP for MCP and 2,6-DCP = 2,5-DCP > 3,4-DCP = 2,4-DCP > 2,3-DCP for DCP.

Dong and Huang [57] reported photocatalytic oxidation reaction pathway for 4CP by $TiO_2/UV/O_2$ process. $OH^•$ attacks the ortho- and para-positions more readily than the meta-position. A series of reactions involving $OH^•$ produces chloro-dihydroxycyciohexadienyl radical which can then react with $OH^•$ to produce 4-CC, 4-chlororesorcinol, and hydroquinone as the major reaction intermediates which can form hydroxyhydroquinone by reaction with $OH^•$. A series of reactions with $OH^•$ finally leads to the formation of CO_2 and H_2O. $OH^•$ attack of a halogenated phenol chlorodihydroxycyclohexadienyl a free radical is formed. This free radical can follow two reaction pathways: (1) hydroxylation without dechlorination and (2) hydroxylation with dechlorination. MCP degradation occurs by first pathway. DCP and TCP can be degraded by both reaction pathways. While, Tet-CP and PCP follow only second reaction pathway. As the chlorine content increases, chlorine, due to its electron-withdrawing nature, decreases e^- density of aromatic ring and chloroorganics reaction ability [58]. The chlorophenolics are converted into inorganic products like CO_2, H_2O and Cl^- by photocatalytic treatment [59].

4.3.5 Catalyst recycling studies

TiO_2 may either be used as a colloidal suspension in the aqueous solution or attached to a support as a fixed film for effluent treatment [60, 61]. The efficiency of catalyst dispersed systems is higher than fixed film system for the degradation of pollutants [62]. But the main problem of these systems is catalyst separation after the treatment and re-dispersion in the next water to be treated. The pH of the effluent, after photocatalytic treatment, drops due to the formation of inorganic acids from the heterogeneous content in organic contaminants [63]. For the catalyst separation, treated effluent was set to pH 7.0 by dilute NaOH solution to attain the zero charge and left for 5 h for catalyst sedimentation [63, 64]. About 94% catalyst was recovered by this process while the remaining 6% was lost. Fernandez-Ibanez et al. [63] reported more than 97% catalyst recovery by charge neutralization to the isoelectric point (IEP) of TiO_2 at pH 7.0. The pH of the effluent after TiO_2 sedimentation by charge neutralization is within the permitted disposal range for treated effluent. The small amount of catalyst (6%) present in supernatant effluent can be recovered using microfiltration system prior to water disposal. The recovered catalyst was used in five successive cycles for the degradation of PC paper mill effluent using UV/TiO_2 process. The lost amount was made up by adding fresh catalyst. The effect of catalyst recycling on COD and color removal efficiency was investigated at different intervals of time (1-4 h). There was no significant loss in COD and color removal efficiency after 5 treatment cycles. After 5 cycles, COD removal efficiency declined from 53 to 49% (initial COD = 500 mg/L) while color removal efficiency declined from 88 to 84% (initial color = 812 mg Pt-Co/L) (Figures 4.26 and 4.27).

4.3.6 Treatment process economic analysis

Although AOPs have been shown to be efficient for the oxidation of persistent organic pollutants, they may require substantial energy consumption for running UV lamps that supply photons to the system [65]. Conversely, several AOPs can be carried out using solar light, because the sun supplies photons having the wavelength necessary for these processes [66]. Solar light is a clean and renewable energy resource.

In this section a comparative economical analysis of UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes has been carried out with two energy approaches: (1) electricity (UV lamps) and (2) solar energy. These processes have been used for the treatment of PC paper mill effluent and the corresponding COD removal (%) has been studied with the treatment time. COD (initial 500 mg/L) has been considered as an indicator of pollution load reduction. The removal of 40% COD from 1 m^3 PC paper mill effluent has been considered as a functional unit for comparing all the processes (electricity and solar driven). The functional unit is based on the same amount of COD removed from the same volume of effluent (1 m^3) [65]. The costs associated with various treatment inputs are mentioned in Table 4.20. The amount of energy, chemicals consumed per functional unit, and total treatment cost for different processes are mentioned in Table 4.21. The following factors have been considered for the economic evaluation of different processes:

1. The electrical energy required to run UV lamps.
2. The electrical energy expenditure has been calculated by taking into account the time needed by each process for removing 40% of the initial COD and UV lamp power (18 W × 4). UV/TiO_2 and UV/TiO_2/H_2O_2 processes took 125 and 60 min, respectively, for the removal of 40% of the initial COD (Figure 4.28). Solar/TiO_2 and Solar/TiO_2/H_2O_2 processes were also able to reduce COD (40%) within 160 and 80 min, respectively, using the solar energy with no electricity consumption.
3. TiO_2 recovery (94%) has been considered for all the treatment processes. About 6% of TiO_2 was lost along with the supernatant effluent.
4. It was assumed that H_2O_2 was completely consumed after 40% COD removal.

The treatment costs of removing a certain quantity of COD from the effluent are very high when the processes use electrical energy as compared to those using sun light (Table 4.21). UV/TiO_2 process was found to be having the higher treatment cost as compared to UV/TiO_2/H_2O_2 process. The solar radiation based processes, i.e. Solar/TiO_2 and Solar/TiO_2/H_2O_2, involve only consumption of chemical products (TiO_2 and H_2O_2) as compared to UV/TiO_2 and UV/TiO_2/H_2O_2 processes which simultaneously consume both the electricity and chemicals. The avoidance of electricity consumption in Solar/TiO_2 and Solar/TiO_2/H_2O_2 processes leads to the treatment cost reduction. The environmental impact (e.g. global warming potential) of manufacturing and distributing the chemicals is one to two orders of magnitude lower than that of generating the electricity [65]. Hence, the environmental impact by UV/TiO_2 and UV/TiO_2/H_2O_2 processes is very high as compared to Solar/TiO_2 and Solar/TiO_2/H_2O_2 processes. There is no significant difference in COD removal efficiency by Solar/TiO_2 (46%) and Solar/TiO_2/H_2O_2 (54%) processes as compared to UV/TiO_2 (49%) and UV/TiO_2/H_2O_2 (59%) processes after 4 h of treatment (Figure 4.28). Hence, solar radiation based treatment processes can be used effectively with minimal treatment cost for paper mill effluent remediation. On the basis of pollutants removal efficiency and economic analysis, Solar/TiO_2/H_2O_2 process could be used effectively for paper mill effluent treatment. But further research is needed for large scale industrial applications.

Table 4.1 XRD diffraction peaks of TiO_2 reported in the literature

Catalyst	Anatase (2θ°)	Rutile (2θ°)	Reference
Synthesized TiO_2	25.3, 36.9, 37.8, 38.6, 48.0, 53.9, 55.1	27.5, 36.2	[67]
Pure TiO_2 and Ln(III)-TiO_2 (Ln = Tb, Eu, Sm)	25.17, 37.77, 48.03, 55.08, 62.56	27.4	[68]
TiO_2-P25 and Ag-TiO_2	25.2, 38, 48.2, 55, 62.5	27.5, 36, 54, 69	[69]
TiO_2-P25 and synthesized TiO_2	25.3, 37.8, 48, 53.9, 55	27.6	[70]
Anatase and TiO_2/sepiolite	25.3, 37.9, 48.1	27.4	[71]

Table 4.2 FTIR peaks/bands of TiO_2 reported in the literature

Catalyst	Peaks/bands (cm^{-1})	Comments	Reference
Pure TiO_2 and Ln(III)-TiO_2 (Ln = Tb, Eu, Sm)	400-1000	Ti-O stretching vibration modes in anatase	[68]
	1633, 3436	OH binding, adsorbed H_2O stretching modes	
TiO_2-P25 and synthesized TiO_2	3100-3600	O-H vibration of Ti-OH groups and H_2O molecules	[72]
	3500	O-H vibration of Ti-OH groups	
	1600	Bending mode of OH groups	
	400-800	Stretching mode of Ti-O	
Synthesized TiO_2	1624	H-O-H binding vibration	[73]
	3372	O-H stretching vibration	
	1405, 410-1000	Ti-O-Ti stretching vibration	

Table 4.3 Analytical characteristics of PC paper mill effluents used for optimization studies

Sample	Parameter	Value (average)
1.	COD (mg/L)	912.7
2.	BOD (mg/L)	228.3
3.	Color (mg Pt-Co/L)	1678.5
4.	pH	7.5

Table 4.4 Average analytical characteristics of pulp bleaching effluents

Bleaching Stage	BOD (mg/L)	COD (mg/L)	BOD/COD ratio	Color (mg/L Pt-Co)	AOX (mg/L)	pH
D/CED Sequence						
D/C	78	371	0.21	353	57.9	1.9
E	148	780	0.19	1887	20.0	10.5
D	73	120	0.61	40	6.7	3.5
DED Sequence						
D_1	253	1053	0.24	1040	21.3	3.4
E	205	853	0.24	1227	18.7	11.5
D_2	60	200	0.30	86	4.7	3.5
DE_PD Sequence						
D_1	212	813	0.26	980	18.0	3.3
E_P	168	673	0.25	1113	15.3	10.5
D_2	53	155	0.34	75	3.3	3.3
ODED Sequence						
D_1	120.6	430.8	0.28	121.8	10.7	3.5
E	98.6	340.1	0.29	133.3	9.3	11.4
D_2	50.5	105.8	0.48	62.4	2.6	3.2

Table 4.5 Chlorophenolics removal (%) for D/C and E stage effluents of D/CED sequence using UV/TiO_2 and UV/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (µg/L)		Removal (%)			
				UV/TiO_2		UV/TiO_2/H_2O_2	
		D/C	E^D	D/C	E	D/C	E
1.	3-CP	0.62	1.40	83	38	85	54
2.	4-CP	0.24	0.58	76	46	89	46
3.	2,6-DCP	0.07	0.15	78	48	ND	59
4.	2,5-DCP	8.53	17.52	29	8	37	11
5.	2,4-DCP	3.59	7.44	42	22	51	33
6.	2,3-DCP	0.03	0.02	ND	63	ND	89
7.	3,4-DCP	0.12	0.06	82	73	87	87
8.	4-CG	0.31	0.79	77	42	81	49
9.	2,4,5-TCP	9.11	20.42	39	13	43	21
10.	2,3,6-TCP	0.04	0.03	ND	ND	ND	ND
11.	2,3,5-TCP	0.10	0.08	69	69	80	74
12.	2,4,6-TCP	0.03	0.03	ND	68	ND	80
13.	4,5-DCG	1.49	8.46	47	22	56	27
14.	2,3,4-TCP	0.06	0.29	80	31	82	45
15.	4,6-DCG	1.75	15.02	46	12	55	17
16.	3,6-DCC	13.49	6.22	17	29	26	36
17.	3,5-DCC	1.33	0.76	62	46	67	48
18.	3,4,6-TCG	0.75	3.11	56	29	61	37
19.	3,4,5-TCG	2.12	11.17	45	12	55	23
20.	4,5,6-TCG	1.01	2.22	70	39	73	42
21.	5,6-DCV	0.54	2.54	73	43	83	49
22.	PCP	0.39	0.09	61	ND	68	ND
23.	Tet-CG	2.33	5.99	48	30	53	35
24.	TCS	5.34	25.53	39	13	42	25
25.	Tet-CC	0.76	0.72	56	50	58	52
26.	2,6-DCSA	1.77	9.74	53	21	57	30
Total		**55.92**	**140.38**	**37**	**18**	**44**	**25**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.6 Chlorophenolics removal (%) for D_1 and E stage effluents of DED sequence using UV/TiO_2 and UV/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (µg/L)		Removal (%)			
				UV/TiO_2		UV/TiO_2/H_2O_2	
		D_1^D	E^D	D_1	E	D_1	E
1.	3-CP	0.30	2.83	90	41	93	48
2.	4-CP	0.12	0.86	76	64	89	69
3.	2,6-DCP	0.07	0.01	79	ND	88	ND
4.	2,5-DCP	0.17	0.10	82	88	87	92
5.	2,4-DCP	0.05	0.02	82	90	ND	95
6.	2,3-DCP	0.02	0.01	ND	82	ND	ND
7.	3,4-DCP	ND	0.04	-----	60	-----	69
8.	4-CG	1.45	6.71	54	48	62	57
9.	2,4,5-TCP	0.09	0.08	82	72	87	81
10.	2,3,6-TCP	0.07	ND	73	-----	94	-----
11.	2,3,5-TCP	0.17	ND	73	-----	82	-----
12.	2,4,6-TCP	0.02	0.01	ND	83	ND	ND
13.	4,5-DCG	6.23	6.80	43	40	51	52
14.	2,3,4-TCP	0.08	0.07	76	78	91	ND
15.	4,6-DCG	0.09	0.07	88	84	95	94
16.	3,6-DCC	2.47	1.83	56	63	64	72
17.	3,5-DCC	0.77	0.72	77	80	88	86
18.	3,4,6-TCG	0.06	0.07	ND	70	ND	74
19.	3,4,5-TCG	0.02	0.03	80	68	86	88
20.	4,5,6-TCG	0.03	0.12	ND	63	ND	70
21.	5,6-DCV	0.07	0.06	71	65	84	66
22.	PCP	0.08	0.07	97	74	ND	82
23.	Tet-CG	0.08	0.09	76	71	86	77
24.	TCS	0.06	ND	ND	-----	ND	-----
25.	Tet-CC	0.30	0.24	74	69	83	73
26.	2,6-DCSA	0.39	1.04	60	30	67	37
	Total	**13.25**	**21.87**	**55**	**48**	**63**	**57**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.7 Chlorophenolics removal (%) for D_1 and E_P stage effluents of DE_PD sequence using UV/TiO_2 and UV/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (µg/L)		Removal (%)			
				UV/TiO_2		UV/TiO_2/H_2O_2	
		D_1^D	E_P^D	D_1	E_P	D_1	E_P
1.	3-CP	0.11	1.35	92	56	97	64
2.	4-CP	0.04	0.02	81	87	96	ND
3.	2,6-DCP	0.04	ND	86	-----	ND	-----
4.	2,5-DCP	0.13	0.61	93	89	89	92
5.	2,4-DCP	0.01	0.02	84	92	91	ND
6.	2,3-DCP	ND	ND	-----	-----	-----	-----
7.	3,4-DCP	0.04	0.04	77	75	79	81
8.	4-CG	1.56	4.39	58	52	65	59
9.	2,4,5-TCP	0.09	0.07	86	87	93	97
10.	2,3,6-TCP	ND	ND	-----	-----	-----	-----
11.	2,3,5-TCP	ND	ND	-----	-----	-----	-----
12.	2,4,6-TCP	ND	ND	-----	-----	-----	-----
13.	4,5-DCG	4.12	6.00	47	46	54	55
14.	2,3,4-TCP	0.06	0.06	79	84	93	95
15.	4,6-DCG	0.03	0.06	ND	90	ND	95
16.	3,6-DCC	2.14	ND	59	-----	66	-----
17.	3,5-DCC	0.62	ND	83	-----	91	-----
18.	3,4,6-TCG	ND	ND	-----	-----	-----	-----
19.	3,4,5-TCG	0.01	ND	82	-----	ND	-----
20.	4,5,6-TCG	ND	0.05	-----	ND	-----	ND
21.	5,6-DCV	ND	0.06	-----	74	-----	78
22.	PCP	ND	ND	-----	-----	-----	-----
23.	Tet-CG	ND	ND	-----	-----	-----	-----
24.	TCS	ND	ND	-----	-----	-----	-----
25.	Tet-CC	0.25	0.18	83	90	88	ND
26.	2,6-DCSA	ND	0.22	-----	83	-----	86
Total		**9.25**	**13.13**	**57**	**53**	**64**	**61**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.8 Chlorophenolics removal (%) for D_1 and E stage effluents of ODED sequence using UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes

S. No.	Compound	Ci* (µg/L)		Removal (%)			
				UV/TiO_2		$UV/TiO_2/H_2O_2$	
		D_1	E	D_1	E	D_1	E
1.	3-CP	0.16	0.12	81	86	85	89
2.	4-CP	0.04	0.03	85	96	97	ND
3.	2,6-DCP	0.05	0.06	88	82	91	86
4.	2,5-DCP	0.16	0.23	88	75	93	85
5.	2,4-DCP	0.02	0.04	83	79	86	84
6.	2,3-DCP	ND	0.03	-----	ND	-----	ND
7.	3,4-DCP	0.13	0.14	69	65	76	70
8.	4-CG	0.39	3.12	87	56	94	60
9.	2,4,5-TCP	1.13	1.14	72	66	81	77
10.	2,3,6-TCP	ND	0.08	-----	82	-----	ND
11.	2,3,5-TCP	ND	0.19	-----	92	-----	ND
12.	2,4,6-TCP	0.03	ND	ND	-----	ND	-----
13.	4,5-DCG	0.88	11.14	80	28	89	35
14.	2,3,4-TCP	0.07	0.14	80	73	86	77
15.	4,6-DCG	0.05	0.09	ND	84	ND	95
16.	3,6-DCC	3.97	ND	55	-----	61	-----
17.	3,5-DCC	2.06	ND	61	-----	68	-----
18.	3,4,6-TCG	0.13	ND	91	-----	ND	-----
19.	3,4,5-TCG	0.04	ND	ND	-----	ND	-----
20.	4,5,6-TCG	ND	ND	-----	-----	-----	-----
21.	5,6-DCV	0.30	0.33	65	65	73	68
22.	PCP	ND	ND	-----	-----	-----	-----
23.	Tet-CG	ND	ND	-----	-----	-----	-----
24.	TCS	ND	0.19	-----	ND	-----	ND
25.	Tet-CC	0.44	0.26	84	ND	96	ND
26.	2,6-DCSA	0.26	0.28	86	84	ND	93
Total		**10.31**	**17.61**	**66**	**42**	**74**	**49**

ND - not detected; * Initial concentration

Table 4.9 Removal (%) of cRFA for D/C or D_1 and E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences after photocatalysis

Sequence	Compound	Ci* (µg/L)		Removal (%)			
				UV/TiO_2		$UV/TiO_2/H_2O_2$	
		D/C or D_1	E or E_P	D/C or D_1	E or E_P	D/C or D_1	E or E_P
D/CED	CDAA	37.5	124.8	12	2	15	2
	DCDAA	22.2	80.8	20	5	25	8
	TCSA	6.4	58.2	65	12	74	16
	Total	**66.1**	**263.8^D**	**20**	**5**	**24**	**7**
DED	CDAA	33.0	71.0	13	6	19	7
	DCDAA	11.0	51.3	47	9	49	12
	TCSA	6.2	11.9	45	36	52	42
	Total	**50.2^D**	**134.2^D**	**24**	**10**	**29**	**12**
DE_PD	CDAA	25.0	60.1	17	7	23	9
	DCDAA	8.3	32.5	54	11	63	16
	TCSA	4.5	ND	53	-----	60	-----
	Total	**37.8^D**	**92.6^D**	**30**	**9**	**36**	**12**
ODED	CDAA	27.3	60.8	24	12	27	15
	DCDAA	10.2	26.5	63	20	68	24
	TCSA	ND	ND	-----	-----	-----	-----
	Total	**37.5**	**87.3**	**35**	**15**	**38**	**18**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.10 Removal (%) of cFA and cRA for D/C or D_1 and E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences after photocatalysis

Sequence	Compound	Ci* (µg/L)		Removal (%)			
				UV/TiO_2		$UV/TiO_2/H_2O_2$	
		D/C or D_1	E or E_P	D/C or D_1	E or E_P	D/C or D_1	E or E_P
D/CED	cFA	6.4	58.2	65	12	74	16
	cRA	59.8	205.6	15	4	19	4
	Total	**66.2**	**263.8^D**	**20**	**5**	**24**	**7**
DED	cFA	6.2	11.9	45	36	52	42
	cRA	44.1	122.4	22	7	26	9
	Total	**50.3^D**	**134.3^D**	**24**	**10**	**29**	**12**
DE_PD	cFA	4.5	ND	53	-----	60	-----
	cRA	33.4	92.6	26	9	33	12
	Total	**37.9^D**	**92.6^D**	**30**	**9**	**36**	**12**
ODED	cFA	ND	ND	-----	-----	-----	-----
	cRA	37.5	87.4	35	15	38	39
	Total	**37.5**	**87.4**	**35**	**15**	**38**	**18**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.11 Analytical characteristics of PC and BT paper mill (Mill A and Mill B) effluents

S. No.	Parameter	Mill A		Mill B	
		PC effluent	BT effluent	PC effluent	BT effluent
1.	COD (mg/L)	1092	246	549	152
2.	BOD (mg/L)	274	29	185	18
3.	BOD/COD ratio	0.25	0.12	0.34	0.12
4.	Color (Pt-Co mg/L)	2066	1012	959	216
5.	pH	7.5	7.4	7.3	7.1
6.	AOX (mg/L)	15.8	6.6	25.5	17.0

Table 4.12 Concentration of cRFA (μg/L) identified in PC and BT paper mill (Mill A and Mill B) effluents

S. No.	Compound	Mill A (μg/L)		Mill B (μg/L)	
		PC effluent	BT effluent	PC effluent	BT effluent
1.	DCSA	34.3	25.0	12.5	ND
2.	CDAA	19.7	16.4	4.3	3.7
3.	DCDAA	11.8	ND	13.4	0.6
4.	TCSA	17.0	20.7	27.6	18.9
Total		**82.8**	**62.1**	**57.8**	**23.3**

ND - not detected

Table 4.13 Concentration of chlorophenolics (µg/L) identified in PC and BT paper mill (Mill A and Mill B) effluents

S. No.	Compound	Mill A (µg/L)		Mill B (µg/L)	
		PC effluent	BT effluent	PC effluent	BT effluent
1.	3-CP	4.80	1.70	0.96	ND
2.	4-CP	1.97	0.90	0.36	0.01
3.	2,6-DCP	2.40	1.69	0.75	0.09
4.	2,5-DCP	1.18	1.12	5.54	1.27
5.	2,4-DCP	3.19	1.74	2.31	0.48
6.	2,3-DCP	ND	0.05	ND	ND
7.	3,4-DCP	1.29	0.94	0.14	ND
8.	4-CG	1.22	1.01	0.64	ND
9.	2,4,5-TCP	10.64	3.74	8.22	2.88
10.	2,3,6-TCP	0.13	ND	0.08	ND
11.	2,3,5-TCP	ND	0.04	0.18	0.13
12.	2,4,6-TCP	1.11	0.07	0.05	0.03
13.	4,5-DCG	2.12	1.41	1.03	0.37
14.	2,3,4-TCP	0.20	0.15	0.09	ND
15.	4,6-DCG	1.00	1.73	6.57	0.23
16.	3,6-DCC	0.24	ND	11.31	7.67
17.	3,5-DCC	ND	ND	2.06	ND
18.	3,4,6-TCG	0.87	1.18	0.76	0.36
19.	3,4,5-TCG	ND	ND	2.08	0.34
20.	4,5,6-TCG	0.04	ND	0.69	0.23
21.	5,6-DCV	0.13	ND	0.22	ND
22.	PCP	ND	ND	ND	0.17
23.	Tet-CG	ND	ND	2.98	1.25
24.	TCS	0.07	0.01	7.03	3.92
25.	Tet-CC	ND	ND	1.65	0.75
26.	2,6-DCSA	0.35	0.08	4.05	2.42
Total		**32.96**	**17.56**	**59.73**	**22.59**

ND - not detected

Table 4.14 Chlorophenolics removal (%) for PC effluent of Mill A using UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (μg/L)	Removal (%)			
			UV/TiO_2	UV/TiO_2/H_2O_2	Solar/TiO_2	Solar/TiO_2/H_2O_2
1.	3-CP	2.20	65	73	50	66
2.	4-CP	0.90	74	86	52	74
3.	2,6-DCP	1.10	53	59	45	50
4.	2,5-DCP	0.54	76	ND	72	97
5.	2,4-DCP	1.46	56	64	46	44
6.	2,3-DCP	ND	------	------	------	------
7.	3,4-DCP	0.59	75	86	87	85
8.	4-CG	0.56	68	74	34	71
9.	2,4,5-TCP	4.87	48	53	46	49
10.	2,3,6-TCP	0.06	64	91	36	ND
11.	2,3,5-TCP	ND	------	------	------	------
12.	2,4,6-TCP	0.51	57	70	38	68
13.	4,5-DCG	0.97	67	82	64	78
14.	2,3,4-TCP	0.09	67	ND	83	94
15.	4,6-DCG	0.46	69	88	88	60
16.	3,6-DCC	0.11	72	81	ND	ND
17.	3,5-DCC	ND	------	------	------	------
18.	3,4,6-TCG	0.40	51	66	65	70
19.	3,4,5-TCG	ND	------	------	------	------
20.	4,5,6-TCG	0.02	ND	ND	ND	ND
21.	5,6-DCV	0.06	82	ND	ND	ND
22.	PCP	ND	------	------	------	------
23.	Tet-CG	ND	------	------	------	------
24.	TCS	0.03	ND	ND	ND	ND
25.	Tet-CC	ND	------	------	------	------
26.	2,6-DCSA	0.16	71	84	39	ND
Total		**15.09**	**59**	**68**	**52**	**61**

ND - not detected; * Initial concentration

Table 4.15 Chlorophenolics removal (%) for BT effluent of Mill A using UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (µg/L)	Removal (%)			
			UV/TiO_2	UV/TiO_2/H_2O_2	Solar/TiO_2	Solar/TiO_2/H_2O_2
1.	3-CP	1.70	75	78	71	67
2.	4-CP	0.90	86	91	72	92
3.	2,6-DCP	1.69	64	85	52	82
4.	2,5-DCP	1.12	76	79	80	71
5.	2,4-DCP	1.74	68	71	58	74
6.	2,3-DCP	0.05	80	ND	ND	ND
7.	3,4-DCP	0.94	75	78	75	81
8.	4-CG	1.01	69	76	59	64
9.	2,4,5-TCP	3.74	58	65	50	62
10.	2,3,6-TCP	ND	------	------	------	------
11.	2,3,5-TCP	0.04	ND	ND	ND	ND
12.	2,4,6-TCP	0.07	71	ND	86	ND
13.	4,5-DCG	1.41	65	68	81	68
14.	2,3,4-TCP	0.15	60	87	67	93
15.	4,6-DCG	1.73	74	76	78	88
16.	3,6-DCC	ND	------	------	------	------
17.	3,5-DCC	ND	------	------	------	------
18.	3,4,6-TCG	1.18	67	75	79	71
19.	3,4,5-TCG	ND	------	------	------	------
20.	4,5,6-TCG	ND	------	------	------	------
21.	5,6-DCV	ND	------	------	------	------
22.	PCP	ND	------	------	------	------
23.	Tet-CG	ND	------	------	------	------
24.	TCS	0.01	ND	ND	ND	ND
25.	Tet-CC	ND	------	------	------	------
26.	2,6-DCSA	0.08	ND	ND	75	ND
Total		**17.56**	**68**	**75**	**66**	**73**

ND - not detected; * Initial concentration

Table 4.16 Chlorophenolics removal (%) for PC effluent of Mill B using UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

S. No.	**Compound**	**Ci* (µg/L)**	**Removal (%)**			
			UV/TiO_2	**UV/TiO_2/H_2O_2**	**Solar/TiO_2**	**Solar/TiO_2/H_2O_2**
1.	3-CP	0.87	80	86	74	77
2.	4-CP	0.33	81	84	75	82
3.	2,6-DCP	0.68	60	67	65	70
4.	2,5-DCP	5.05	31	34	28	30
5.	2,4-DCP	2.10	44	47	40	43
6.	2,3-DCP	ND	------	------	------	------
7.	3,4-DCP	0.13	85	ND	94	ND
8.	4-CG	0.58	63	68	59	65
9.	2,4,5-TCP	7.49	29	37	27	31
10.	2,3,6-TCP	0.07	57	62	71	ND
11.	2,3,5-TCP	0.16	74	81	68	75
12.	2,4,6-TCP	0.05	88	ND	90	ND
13.	4,5-DCG	0.94	70	78	66	70
14.	2,3,4-TCP	0.08	69	86	71	85
15.	4,6-DCG	5.98	34	42	33	37
16.	3,6-DCC	10.30	12	15	10	14
17.	3,5-DCC	1.88	62	67	51	57
18.	3,4,6-TCG	0.69	45	57	53	56
19.	3,4,5-TCG	1.89	60	67	53	62
20.	4,5,6-TCG	0.63	62	77	53	59
21.	5,6-DCV	0.20	67	79	63	71
22.	PCP	ND	------	------	------	------
23.	Tet-CG	2.71	58	63	50	57
24.	TCS	6.40	32	36	29	35
25.	Tet-CC	1.50	65	74	58	66
26.	2,6-DCSA	3.69	49	56	46	50
Total		**54.40**	**37**	**43**	**34**	**39**

ND - not detected; * Initial concentration

Table 4.17 Chlorophenolics removal (%) for BT effluent of Mill B using UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (μg/L)	Removal (%)			
			UV/TiO_2	UV/TiO_2/H_2O_2	Solar/TiO_2	Solar/TiO_2/H_2O_2
1.	3-CP	ND	------	------	------	------
2.	4-CP	0.01	ND	ND	ND	ND
3.	2,6-DCP	0.09	ND	ND	ND	ND
4.	2,5-DCP	1.27	79	88	69	74
5.	2,4-DCP	0.48	85	ND	80	97
6.	2,3-DCP	ND	------	------	------	------
7.	3,4-DCP	ND	------	------	------	------
8.	4-CG	ND	------	------	------	------
9.	2,4,5-TCP	2.88	65	71	56	60
10.	2,3,6-TCP	ND	------	------	------	------
11.	2,3,5-TCP	0.13	84	ND	86	ND
12.	2,4,6-TCP	0.03	ND	ND	ND	ND
13.	4,5-DCG	0.37	86	97	82	93
14.	2,3,4-TCP	ND	------	------	------	------
15.	4,6-DCG	0.23	94	ND	87	90
16.	3,6-DCC	7.67	33	37	30	32
17.	3,5-DCC	ND	------	------	------	------
18.	3,4,6-TCG	0.36	93	96	86	ND
19.	3,4,5-TCG	0.34	85	97	86	88
20.	4,5,6-TCG	0.23	88	ND	87	94
21.	5,6-DCV	ND	------	------	------	------
22.	PCP	0.17	71	ND	88	ND
23.	Tet-CG	1.25	62	68	56	63
24.	TCS	3.92	54	61	49	55
25.	Tet-CC	0.75	71	86	63	76
26.	2,6-DCSA	2.42	60	67	52	58
Total		**22.59**	**55**	**61**	**49**	**55**

ND - not detected; * Initial concentration

Table 4.18 cRFA removal (%) for PC and BT effluents of Mill A using UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (µg/L)		Removal (%)							
				UV/TiO_2		UV/TiO_2/H_2O_2		Solar/TiO_2		Solar/TiO_2/H_2O_2	
		PC^D	BT	PC	BT	PC	BT	PC	BT	PC	BT
1.	DCSA	15.7	25.0	33	28	38	32	32	26	34	29
2.	CDAA	9.0	16.4	50	39	53	41	46	36	50	40
3.	DCDAA	5.4	ND	64	-----	68	-----	51	-----	55	-----
4.	TCSA	7.8	20.7	46	30	48	36	39	28	43	33
Total		**37.9**	**62.1**	**44**	**31**	**48**	**35**	**40**	**29**	**43**	**33**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.19 cRFA removal (%) for PC and BT effluents of Mill B using UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

S. No.	Compound	Ci* (µg/L)		Removal (%)							
				UV/TiO_2		UV/TiO_2/H_2O_2		Solar/TiO_2		Solar/TiO_2/H_2O_2	
		PC^D	BT	PC	BT	PC	BT	PC	BT	PC	BT
1.	DCSA	11.4	ND	38	-----	41	-----	34	-----	37	-----
2.	CDAA	3.9	3.7	65	81	68	85	61	78	63	79
3.	DCDAA	12.2	0.6	42	90	45	ND	37	ND	38	ND
4.	TCSA	25.1	18.9	18	38	21	43	12	34	16	41
Total		**52.5**	**23.3**	**32**	**46**	**34**	**51**	**26**	**43**	**29**	**49**

ND - not detected; * Initial concentration; D: Concentration after dilution (500 mg/L of COD)

Table 4.20 The costs associated with various inputs used for PC effluent treatment

S. No.	Inputs	Cost
1.	TiO_2 (Rs/kg)	580*
2.	H_2O_2 (Rs/kg)	46
3.	Electricity (Rs/kWh)	4

* Laboratory grade TiO_2 (High Media).

Table 4.21 The amount of energy and chemicals consumed per functional unit removed by UV/TiO_2, $UV/TiO_2/H_2O_2$, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes

Treatment Process	TiO_2 (kg/m^3)*	Electricity consumed by UV lamp (kWh/m^3)	H_2O_2 (kg/m^3)	Treatment cost (Rs/m^3)
UV/TiO_2	0.03	300	0	1217
$UV/TiO_2/H_2O_2$	0.03	144	1.02	640
Solar/TiO_2	0.03	0	0	17
Solar/TiO_2/H_2O_2	0.03	0	1.02	64

*Catalyst that is lost along with treated effluent and needs to be added for next treatment cycle

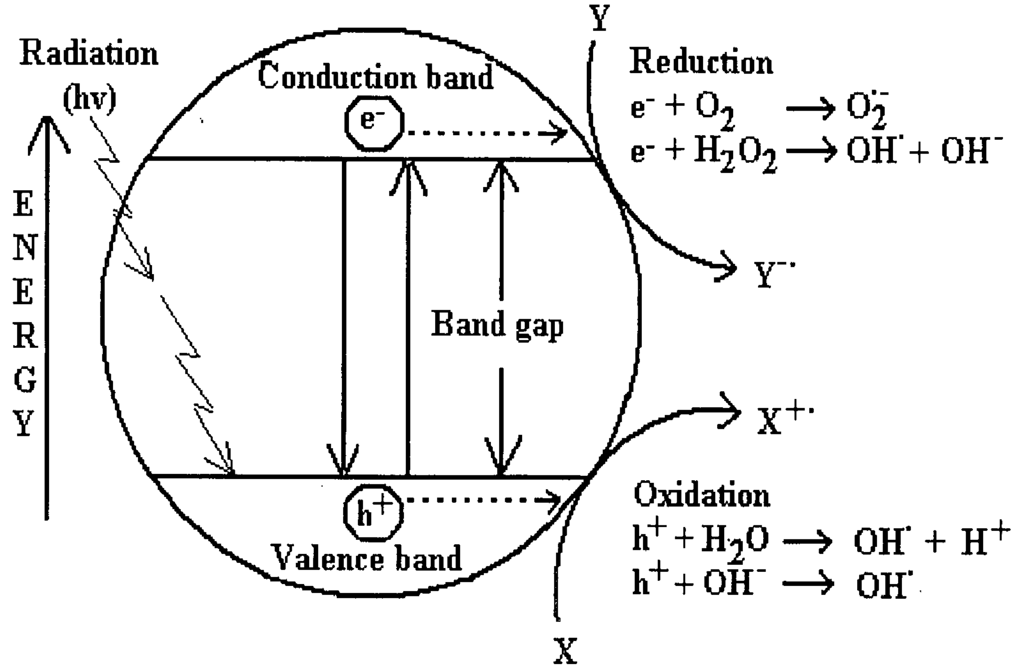


Figure 4.1 Photoexcitation of a TiO_2 semiconductor particle and later processes

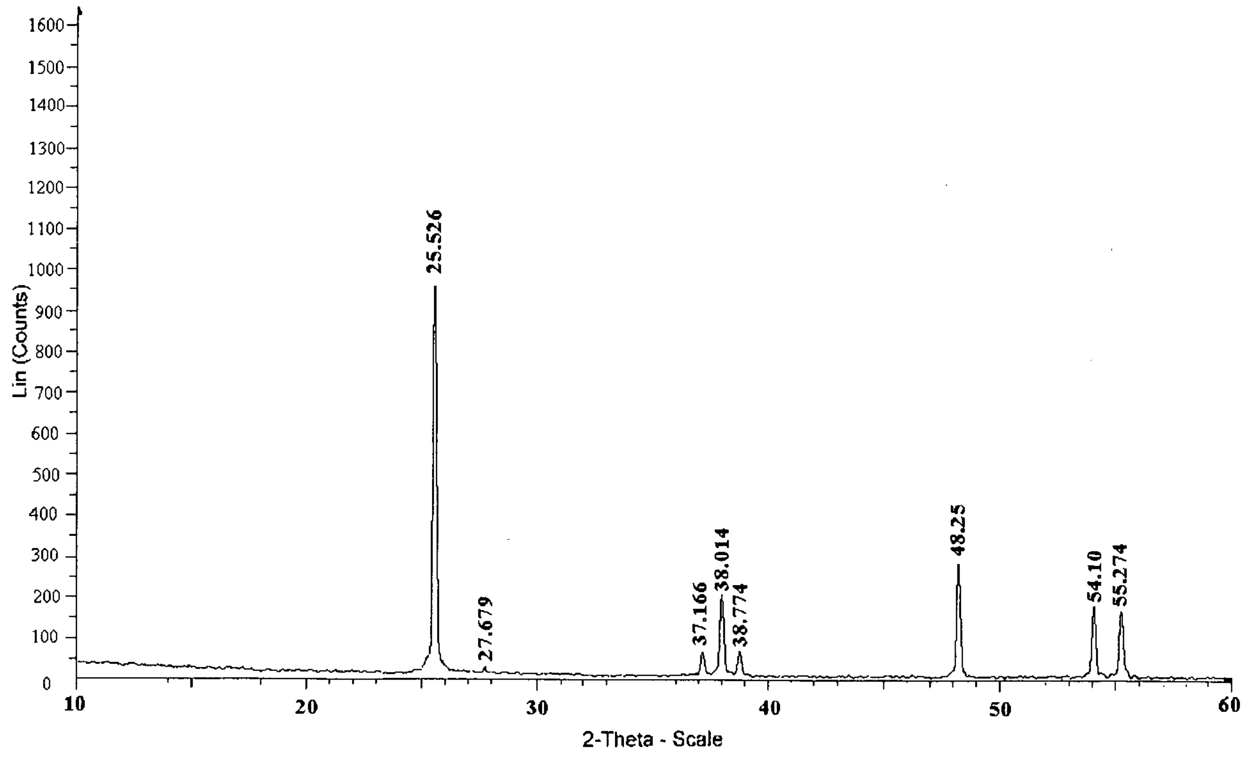
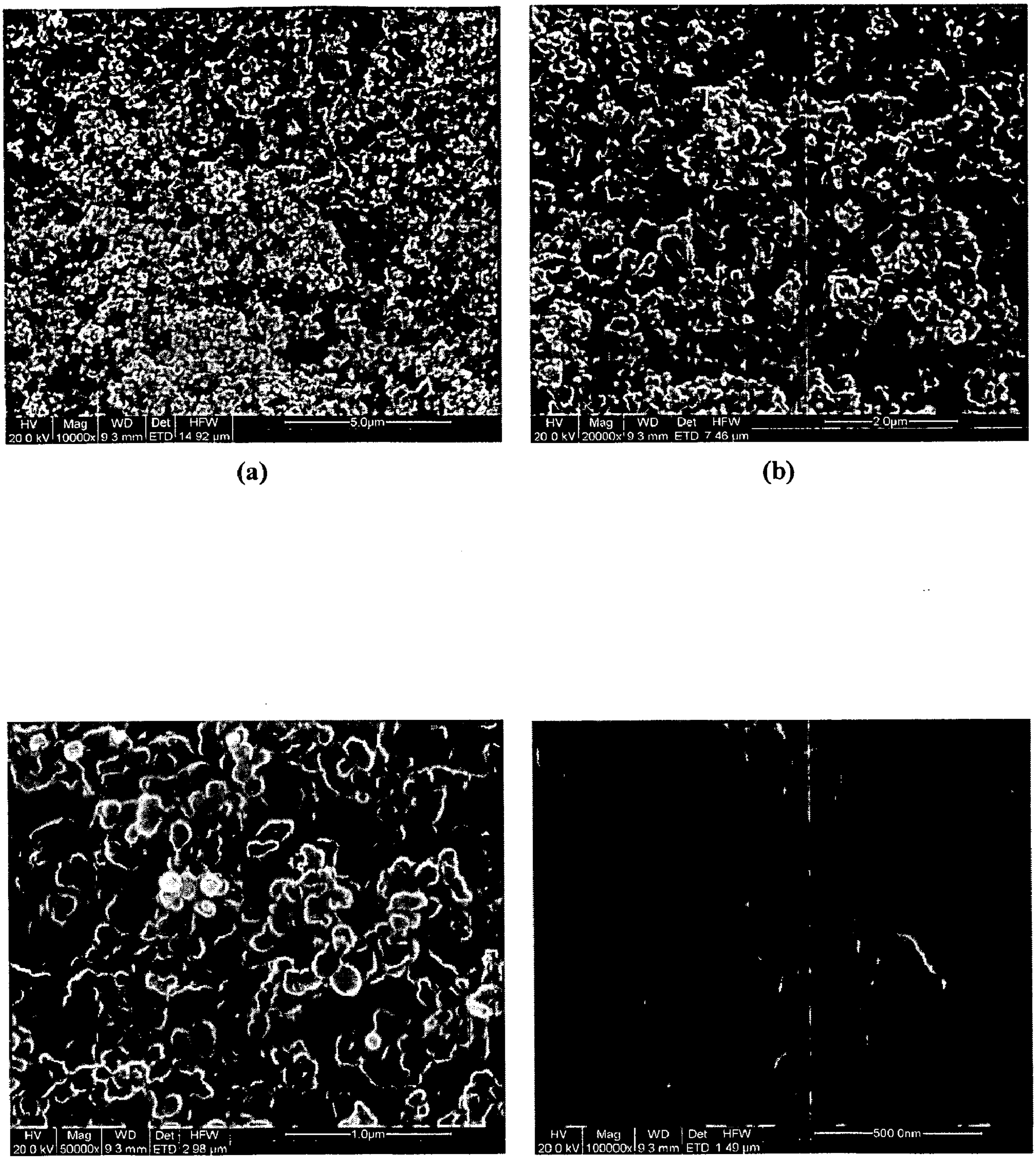


Figure 4.2 XRD pattern of TiO_2



(a)

(b)

(c)

(d)

Figure 4.3 FE-SEM micrographs of TiO_2 at various magnifications: (a) 10,000X, (b) 20,000X, (c) 50,000X, and (d) 100,000X

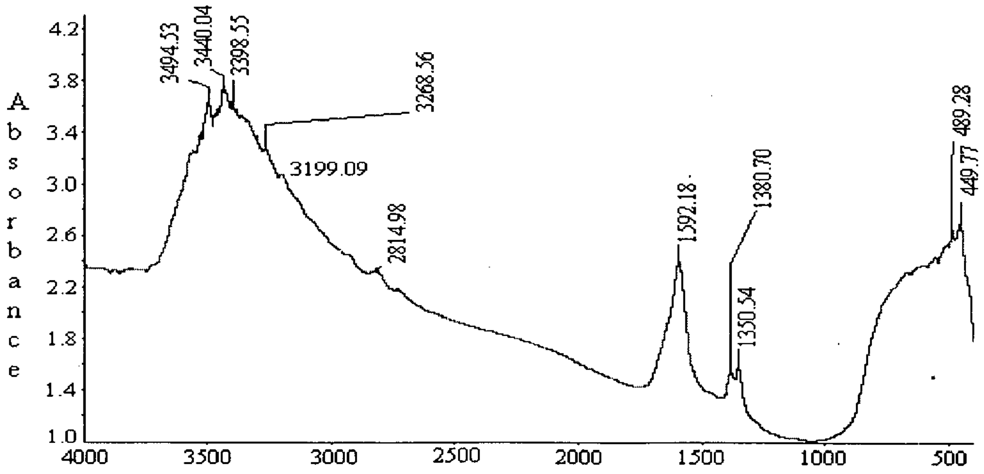


Figure 4.4 FTIR spectra of TiO_2

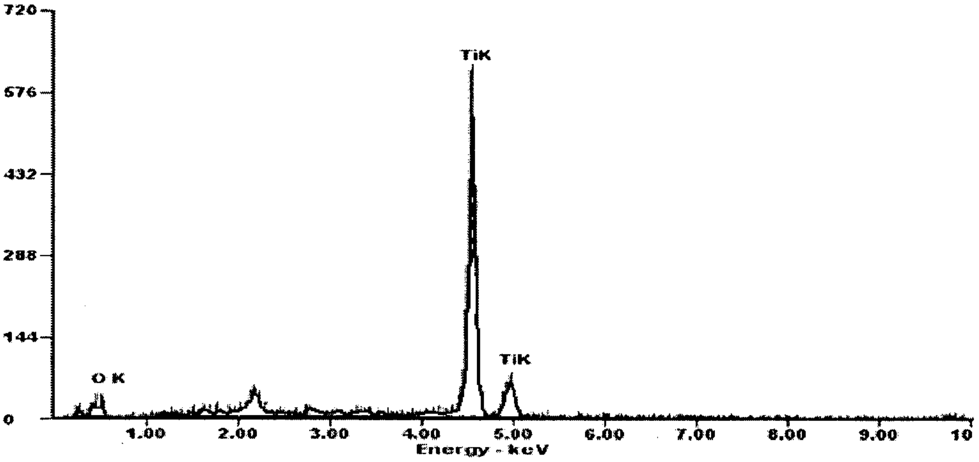


Figure 4.5 EDX spectra of TiO_2

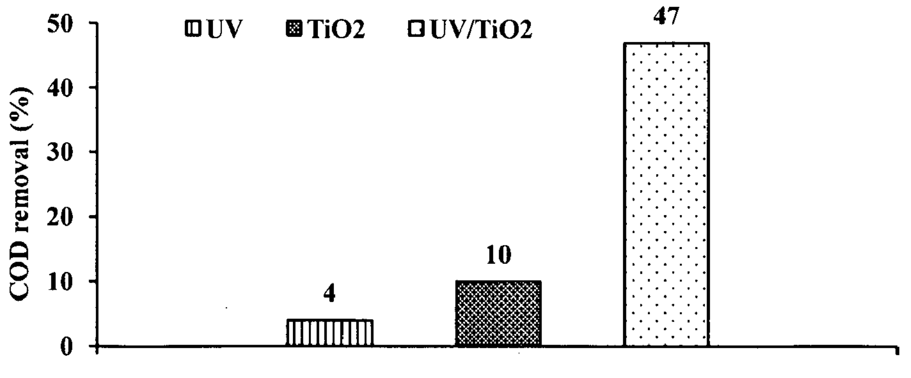


Figure 4.6 Effect of UV photolysis, physical adsorption of organics on TiO_2 surface, and UV/TiO_2 process on COD removal (TiO_2 0.5 g/L, pH 7.0, reaction time 4 h)

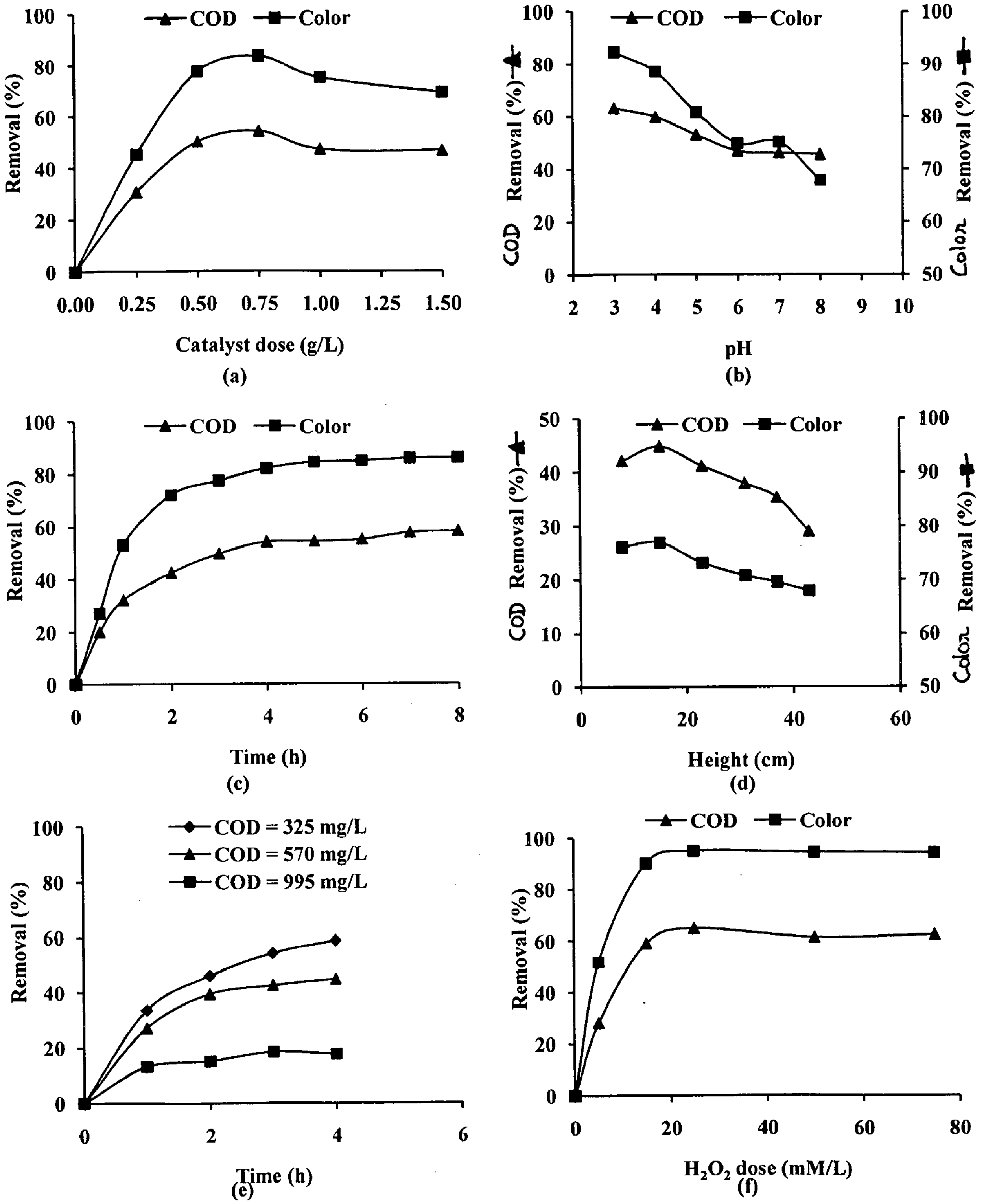


Figure 4.7 Optimization of: (a) Catalyst dose, (b) pH, (c) Reaction time, (d) Light intensity (height), (e) Organic load (COD), and (f) Oxidant (H_2O_2) concentration for the photocatalytic oxidation of PC effluent

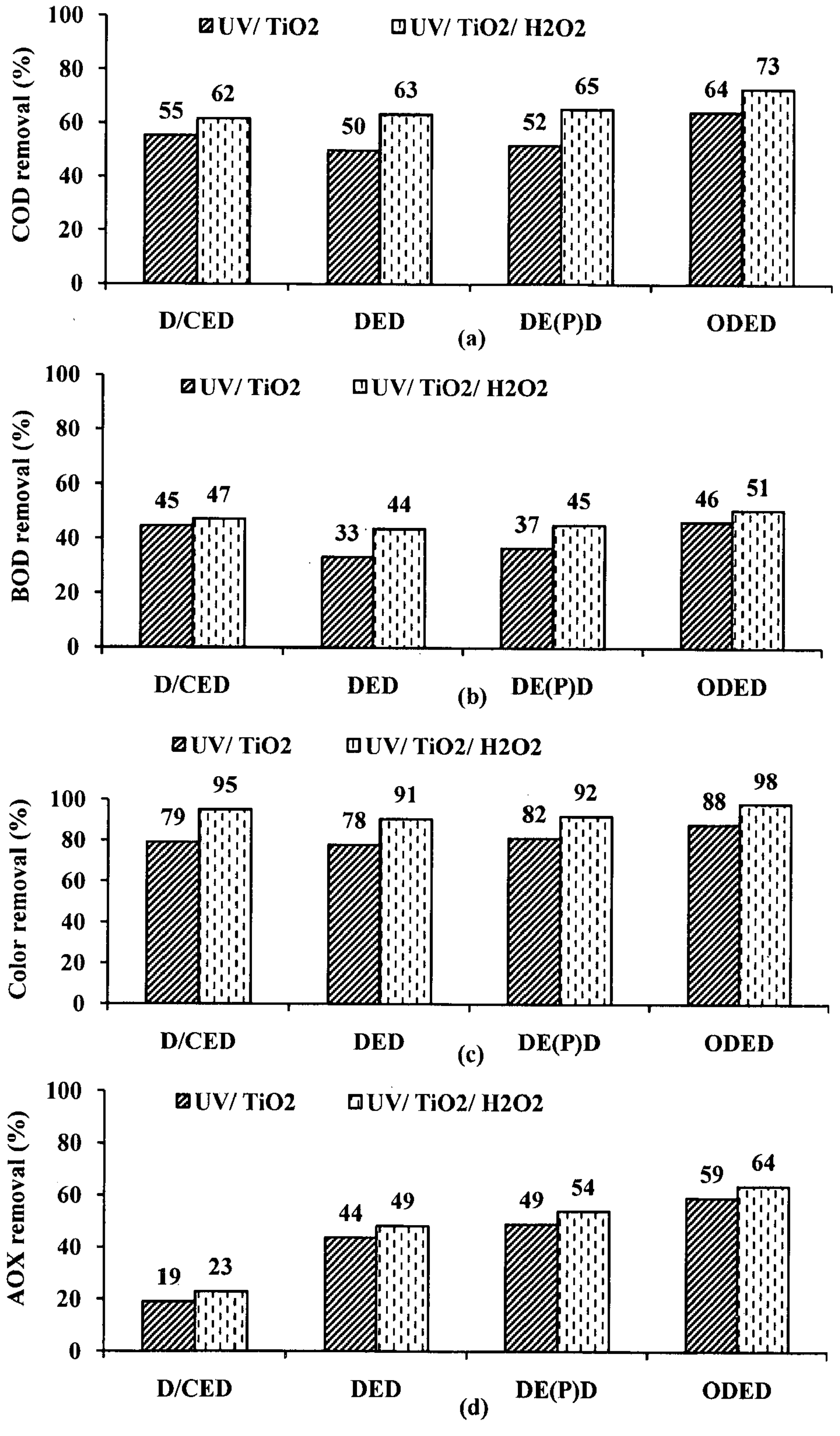


Figure 4.8 Removal (%) of (a) COD, (b) BOD, (c) Color, and (d) AOX for D/C or D_1 stage effluents of D/CED, DED, DE_PD, and ODED sequences by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes

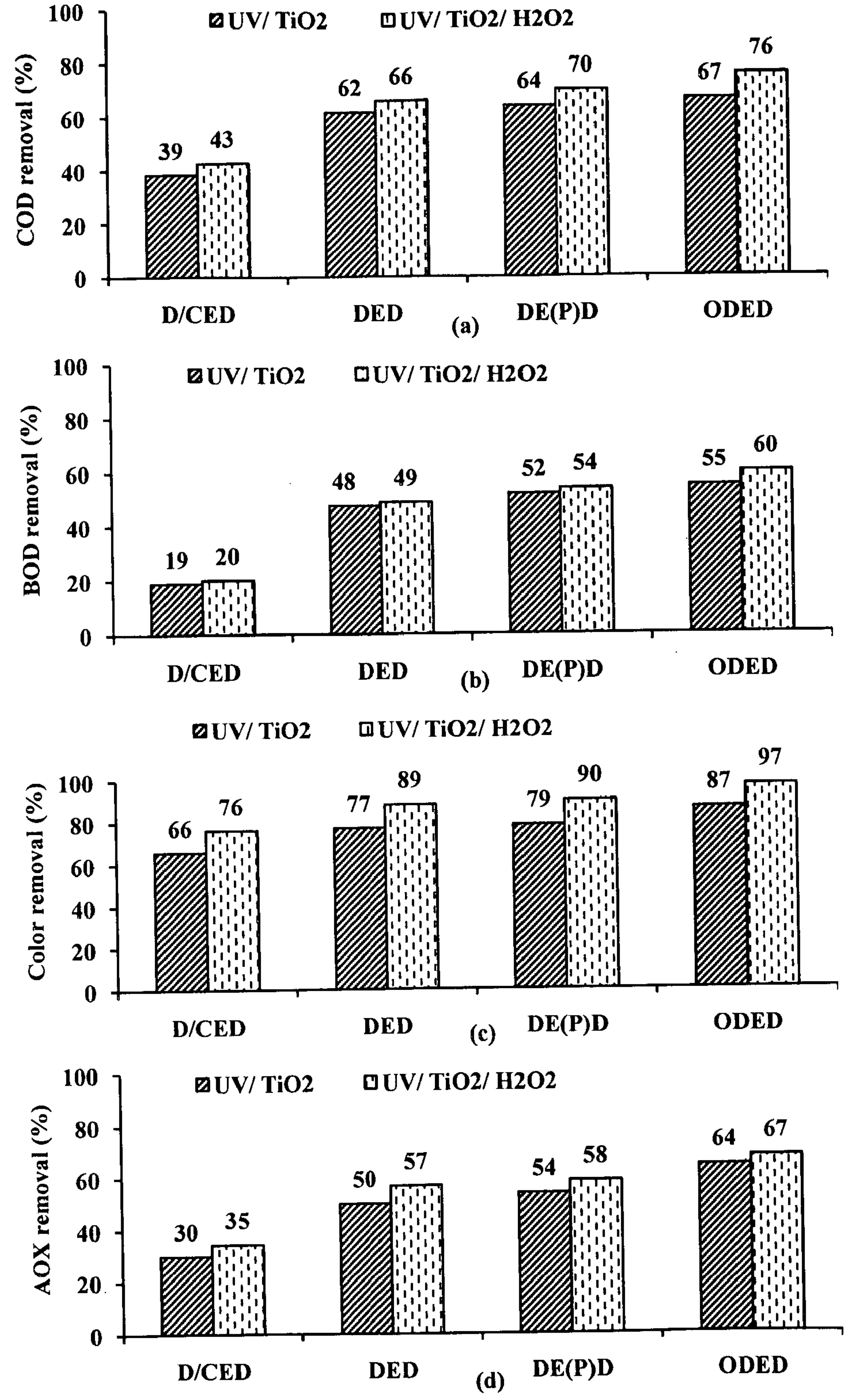
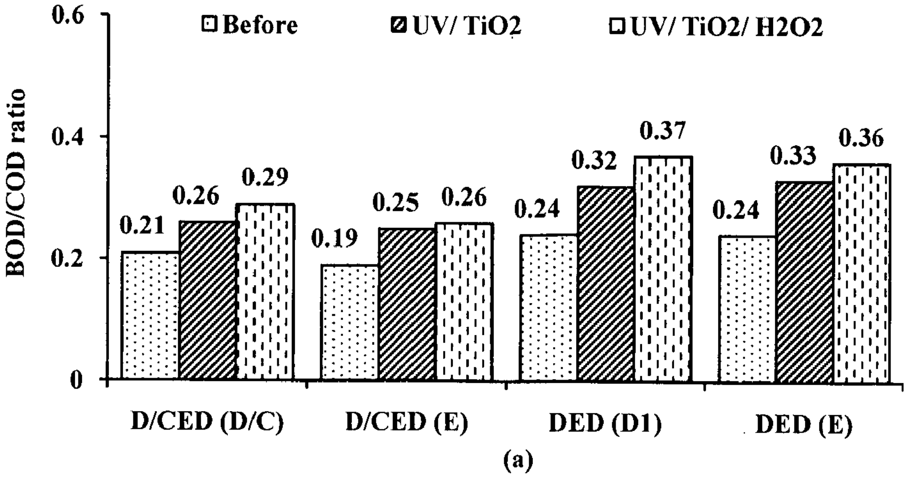


Figure 4.9 Removal (%) of (a) COD, (b) BOD, (c) Color, and (d) AOX for E or E_P stage effluents of D/CED, DED, DE_PD, and ODED sequences by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes



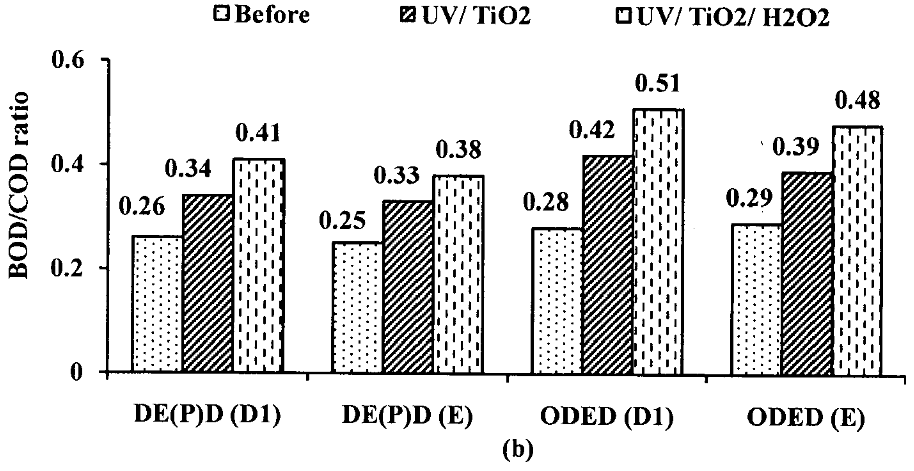


Figure 4.10 Improvement in BOD/COD ratio for D/C or D$_1$ and E or E$_P$ stage effluents of (a) D/CED and DED; (b) DE$_P$D and ODED sequences by UV/TiO$_2$ and UV/TiO$_2$/H$_2$O$_2$ processes

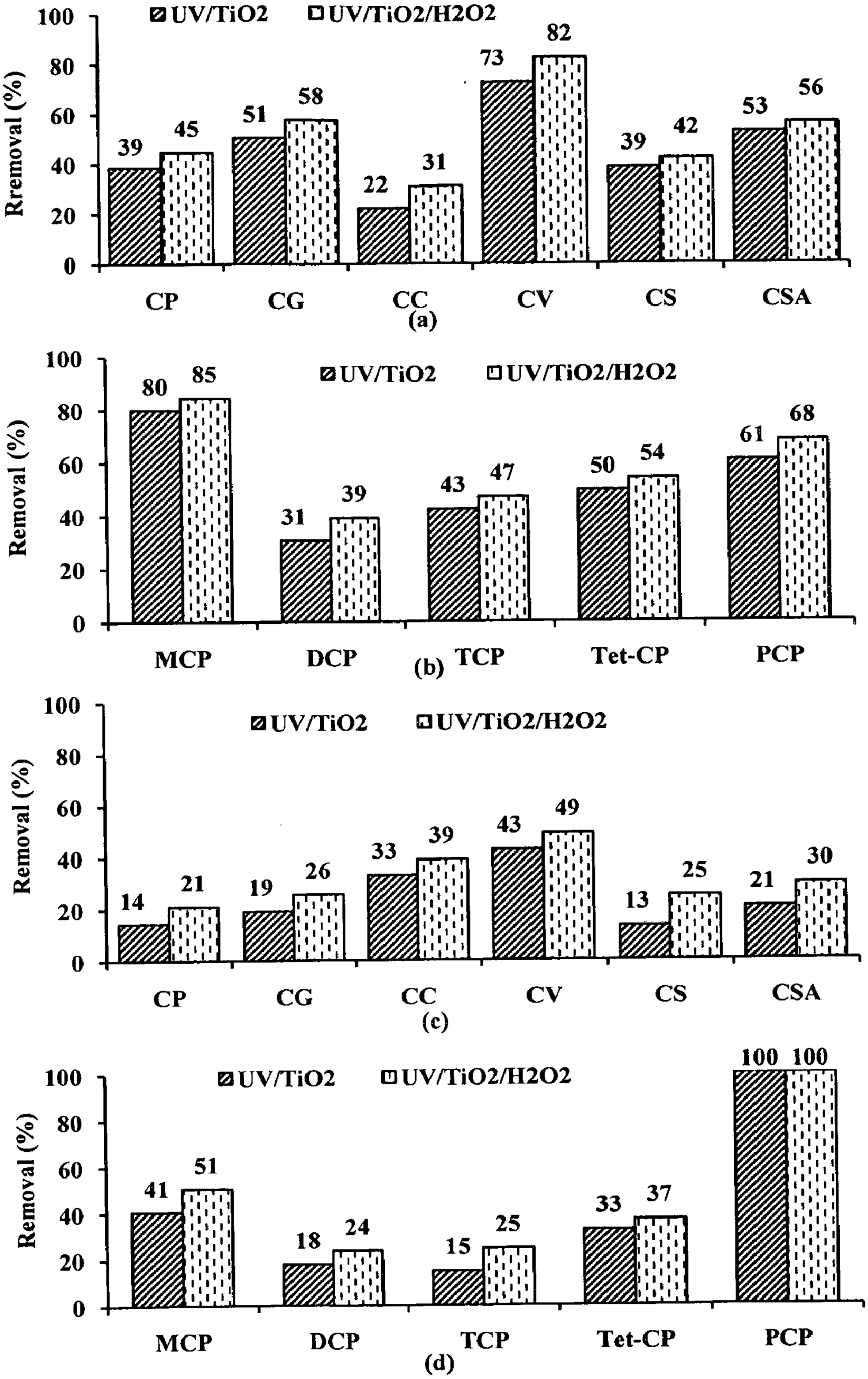


Figure 4.11 Removal (%) of chlorophenolics by chemical family and number of attached chlorine atoms for effluents of different stages: D/C stage (a and b) and E stage (c and d) of D/CED sequence by UV/TiO_2 and UV/TiO_2/H_2O_2 processes

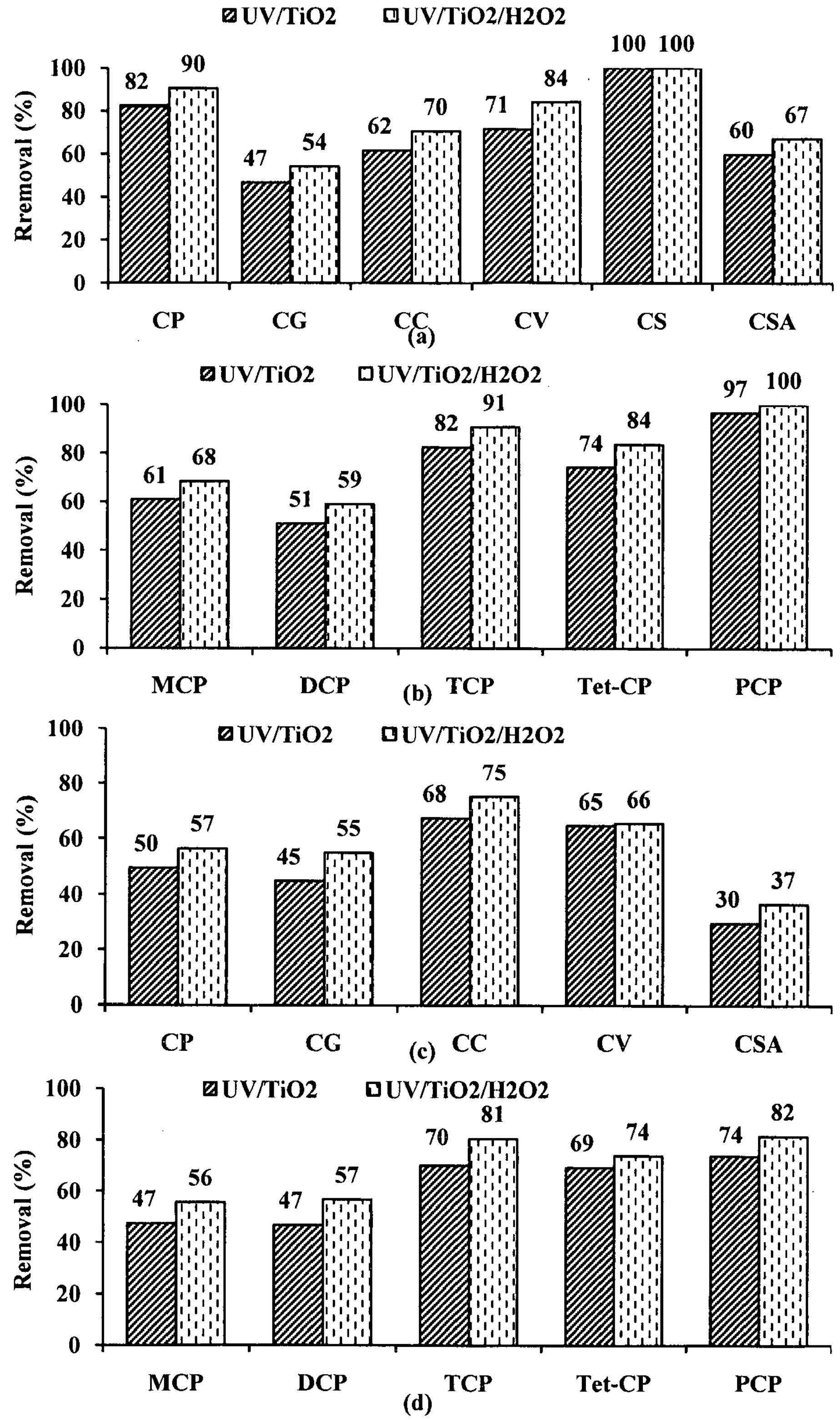


Figure 4.12 Removal (%) of chlorophenolics by chemical family and number of attached chlorine atoms for effluents of different stages: D_1 stage (a and b) and E stage (c and d) of DED sequence by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes

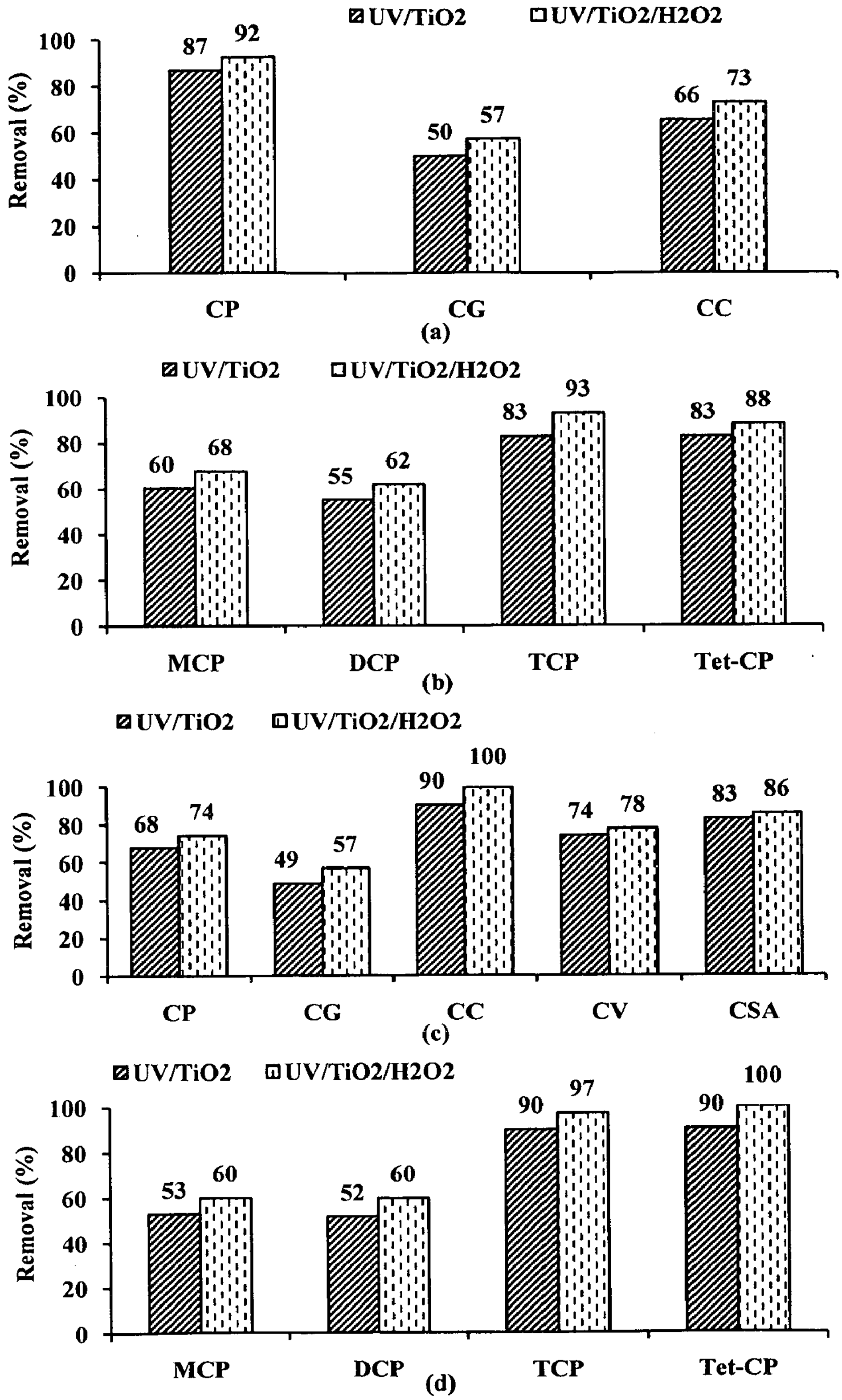


Figure 4.13 Removal (%) of chlorophenolics by chemical family and number of attached chlorine atoms for effluents of different stages: D_1 stage (a-b) and E_P stage (c-d) of DE_PD sequence by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes

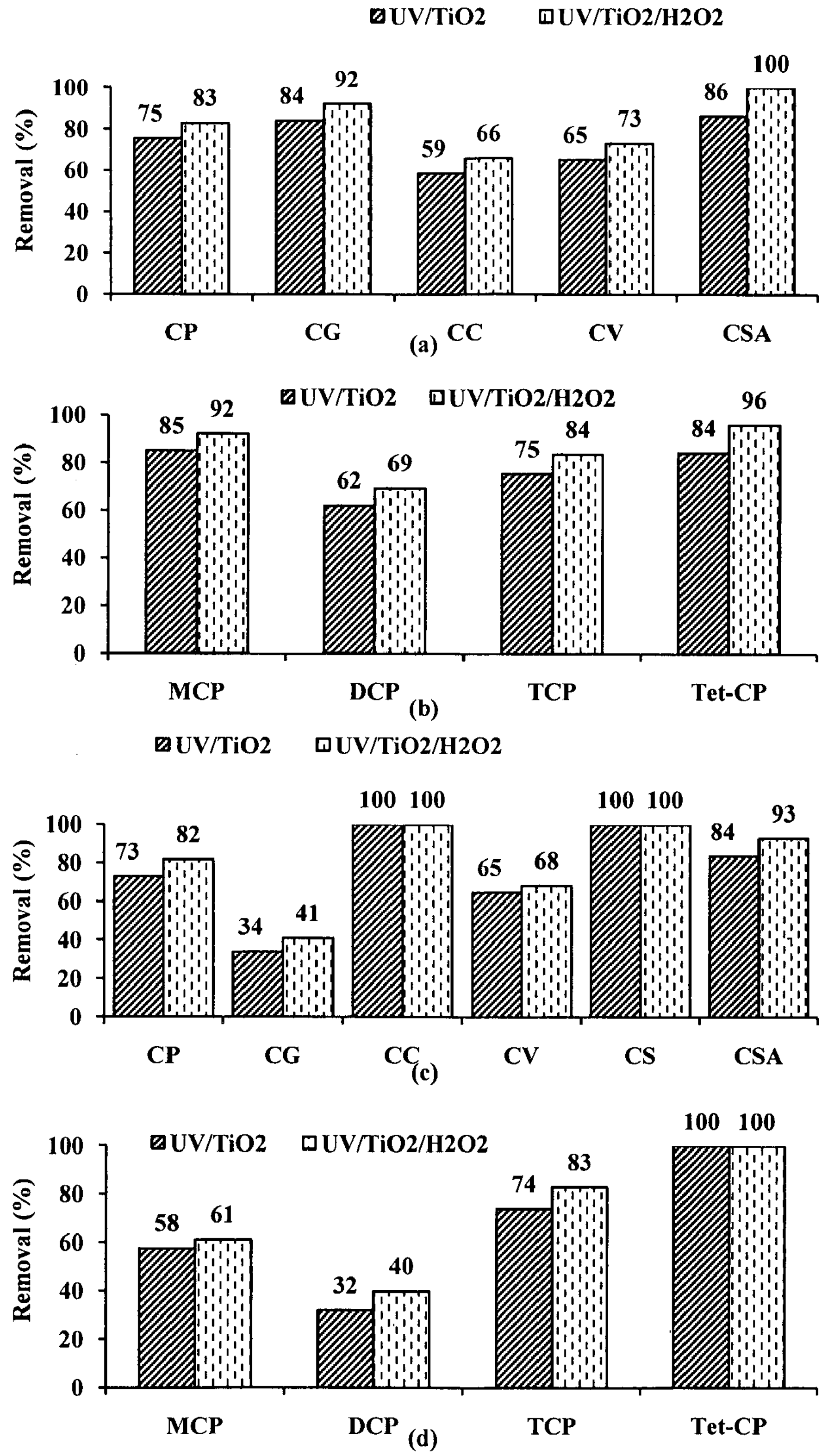


Figure 4.14 Removal (%) of chlorophenolics by chemical family and number of attached chlorine atoms for effluents of different stages: D_1 stage (a and b) and E stage (c and d) of ODED sequence by UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes

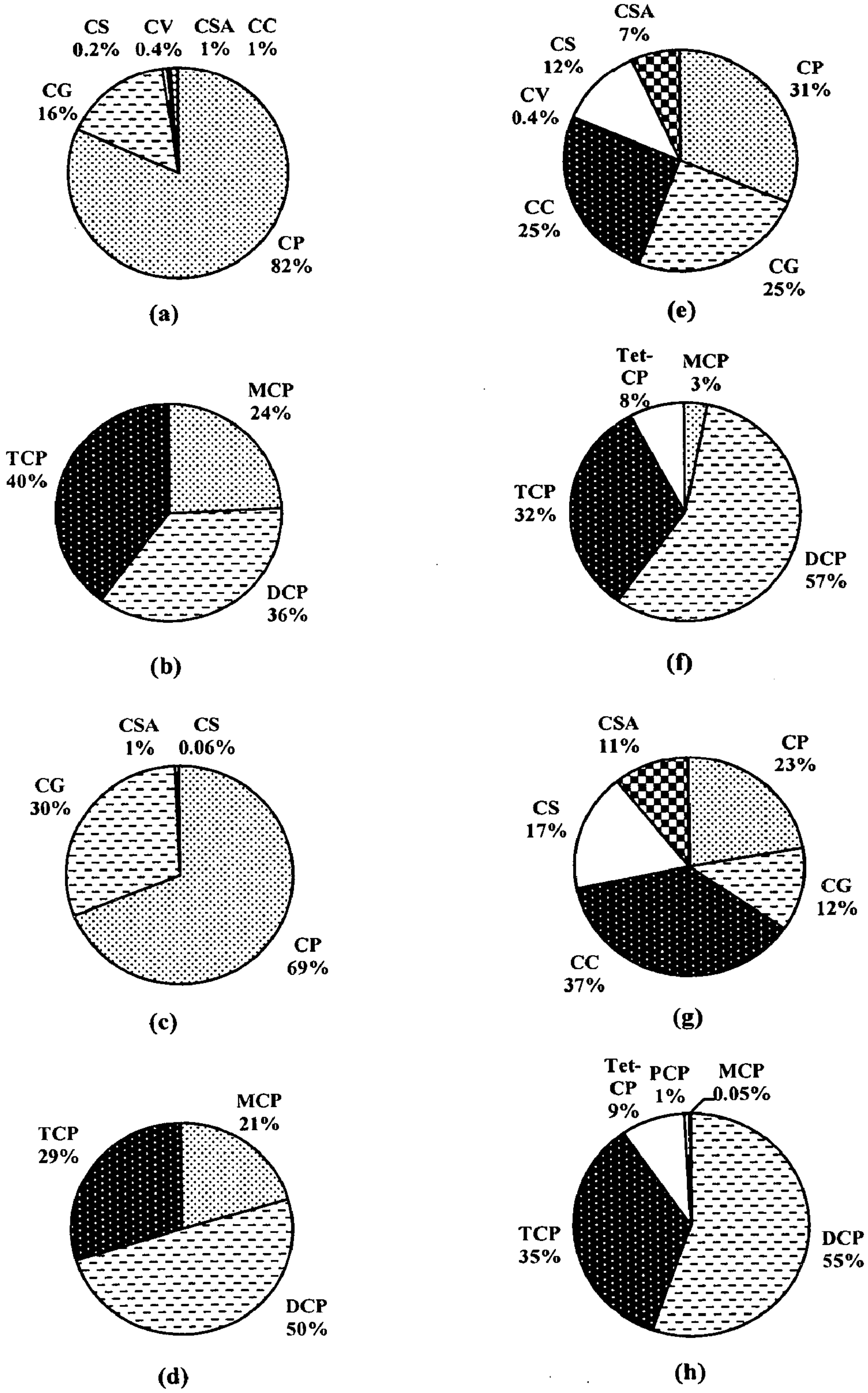


Figure 4.15 Proportion (%) of chlorophenolics by chemical family and number of attached chlorine atoms detected in Mill A: PC (a-b), BT (c-d) and Mill B: PC (e-f), BT (g-h) effluents

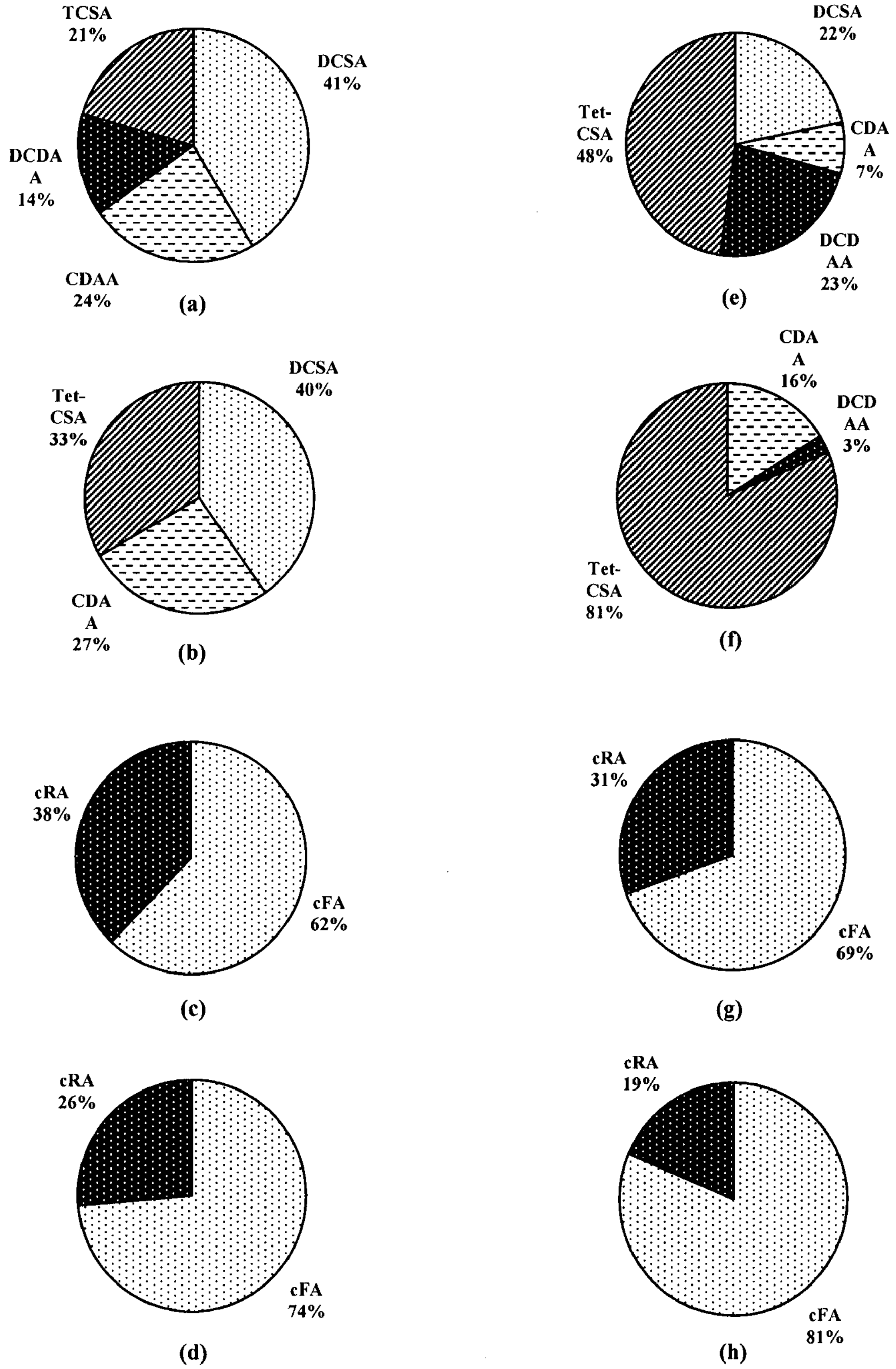


Figure 4.16 Proportion of cRFA detected in Mill A: PC (a, c), BT (b, d) and Mill B: PC (e, g), BT (f, h) effluents

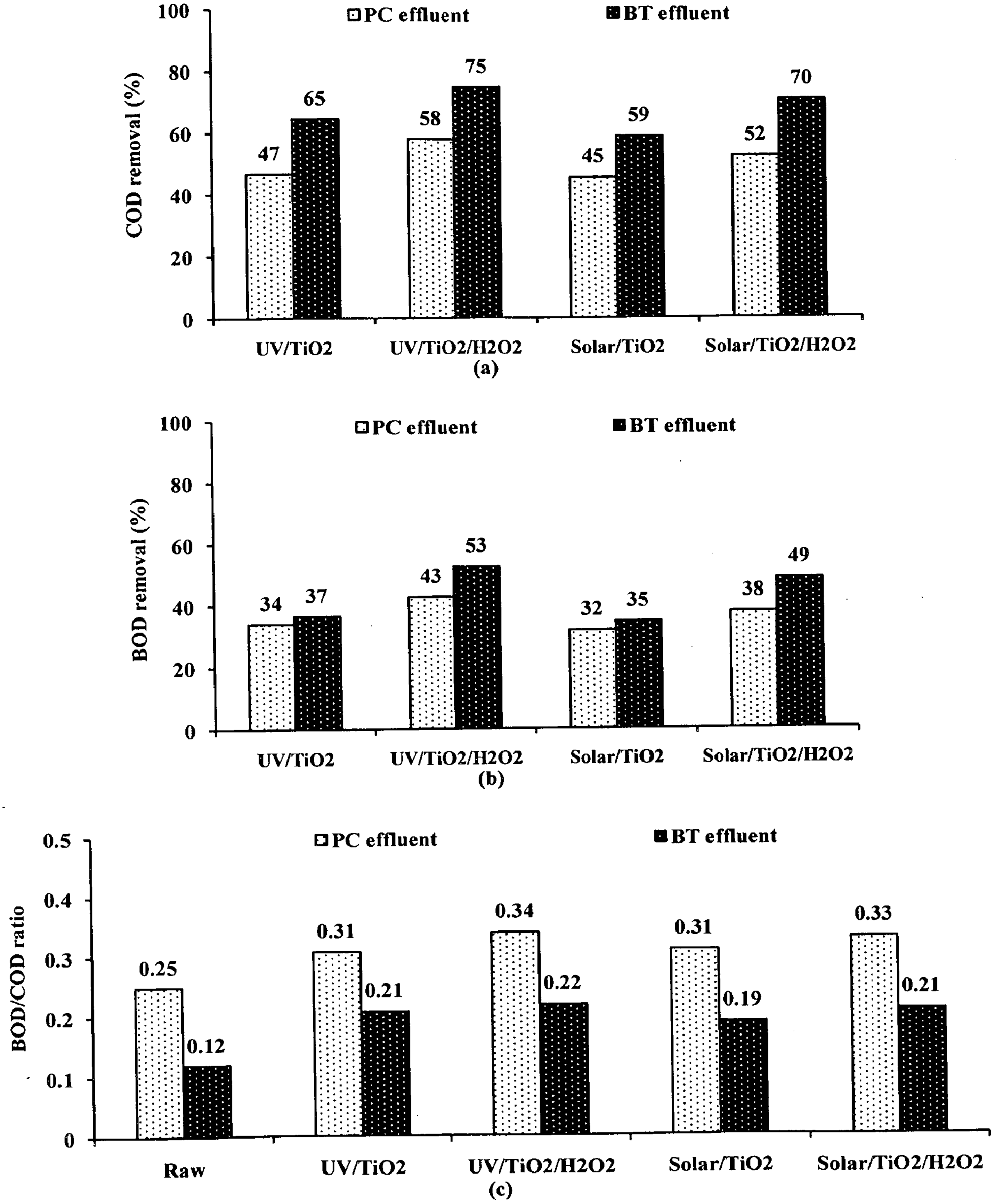
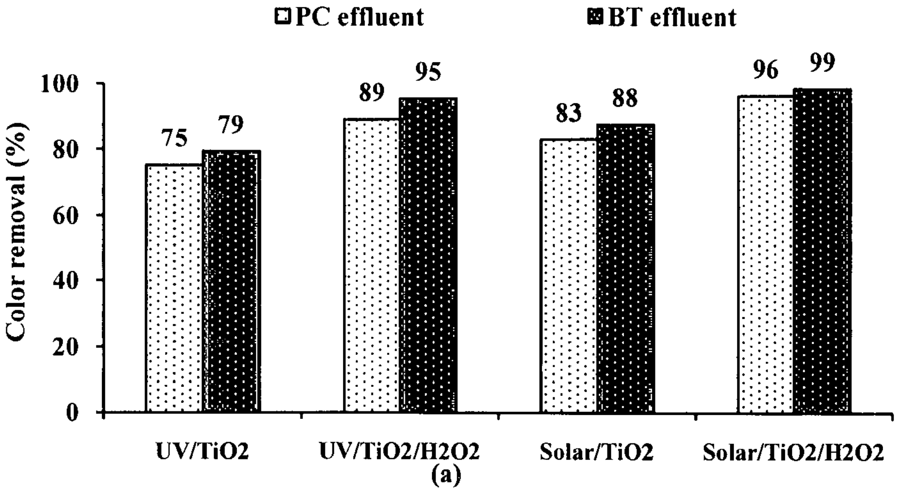


Figure 4.17 Comparison of different treatment processes for the removal (%) of (a) COD, (b) BOD, and (c) BOD/COD ratio improvement for PC and BT effluents of Mill A



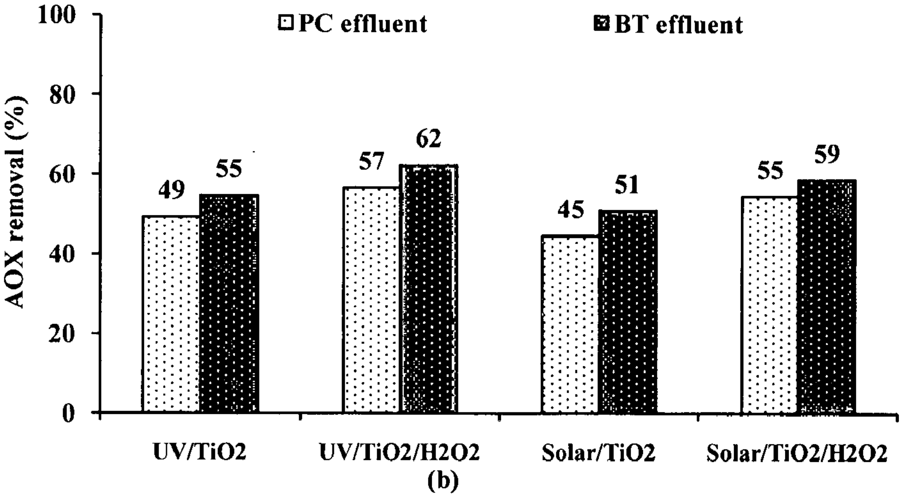


Figure 4.18 Comparison of different treatment processes for the removal (%) of (a) Color and (b) AOX for PC and BT effluents of Mill A

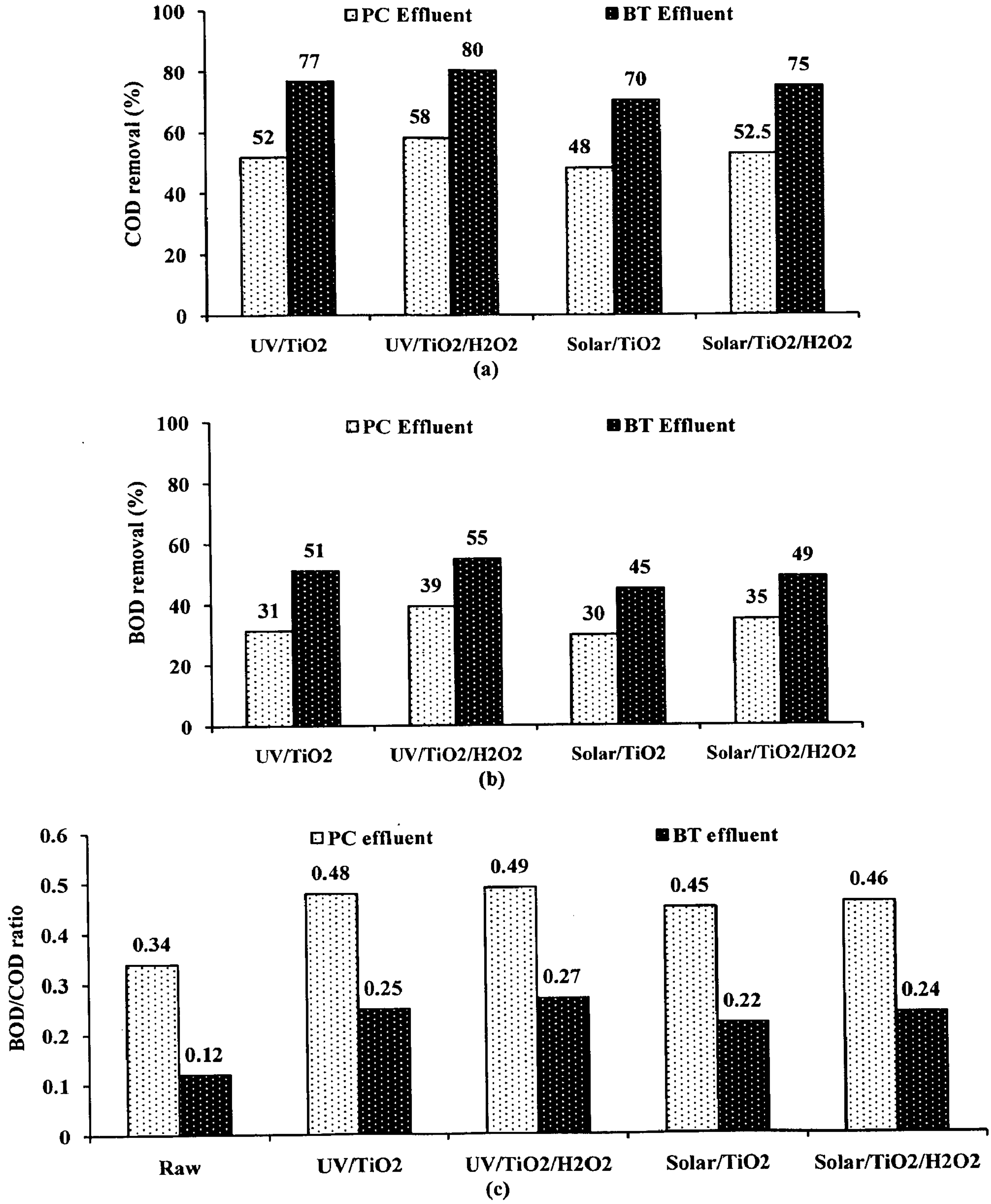
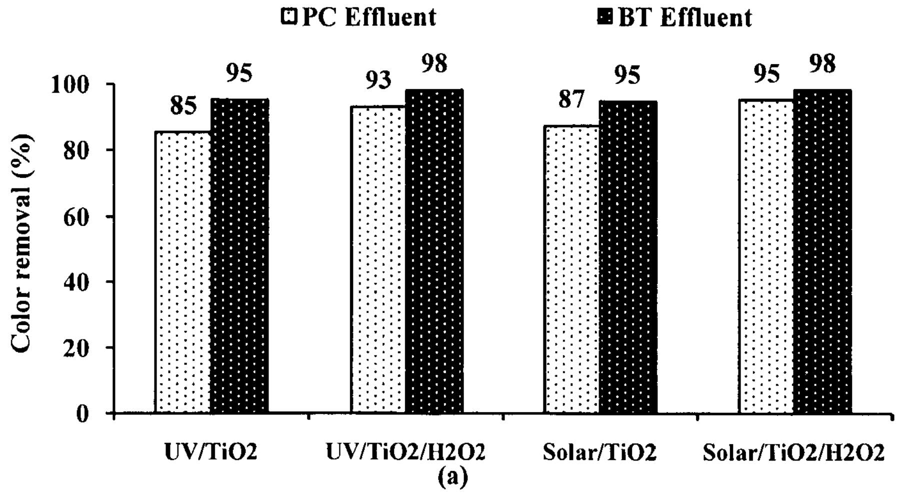


Figure 4.19 Comparison of different treatment processes for the removal (%) of (a) COD, (b) BOD, and (c) BOD/COD ratio improvement for PC and BT effluents of Mill B



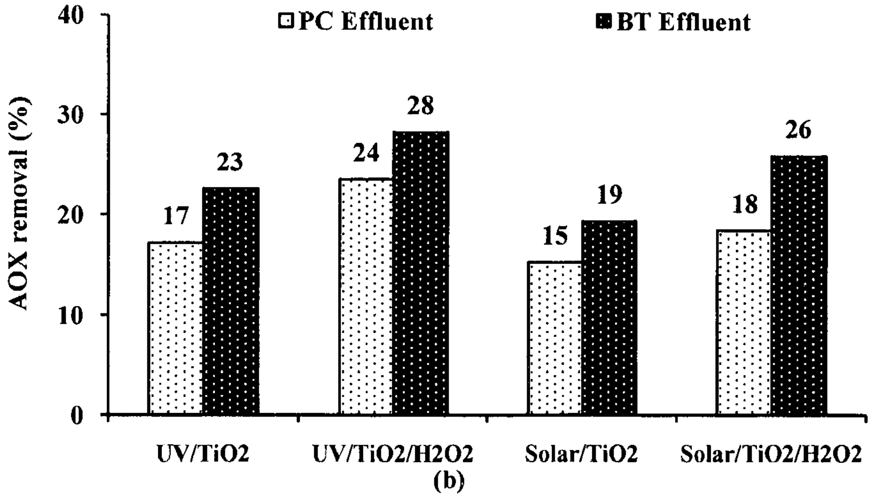


Figure 4.20 Comparison of different treatment processes for the removal (%) of (a) Color and (b) AOX for PC and BT effluents of Mill B

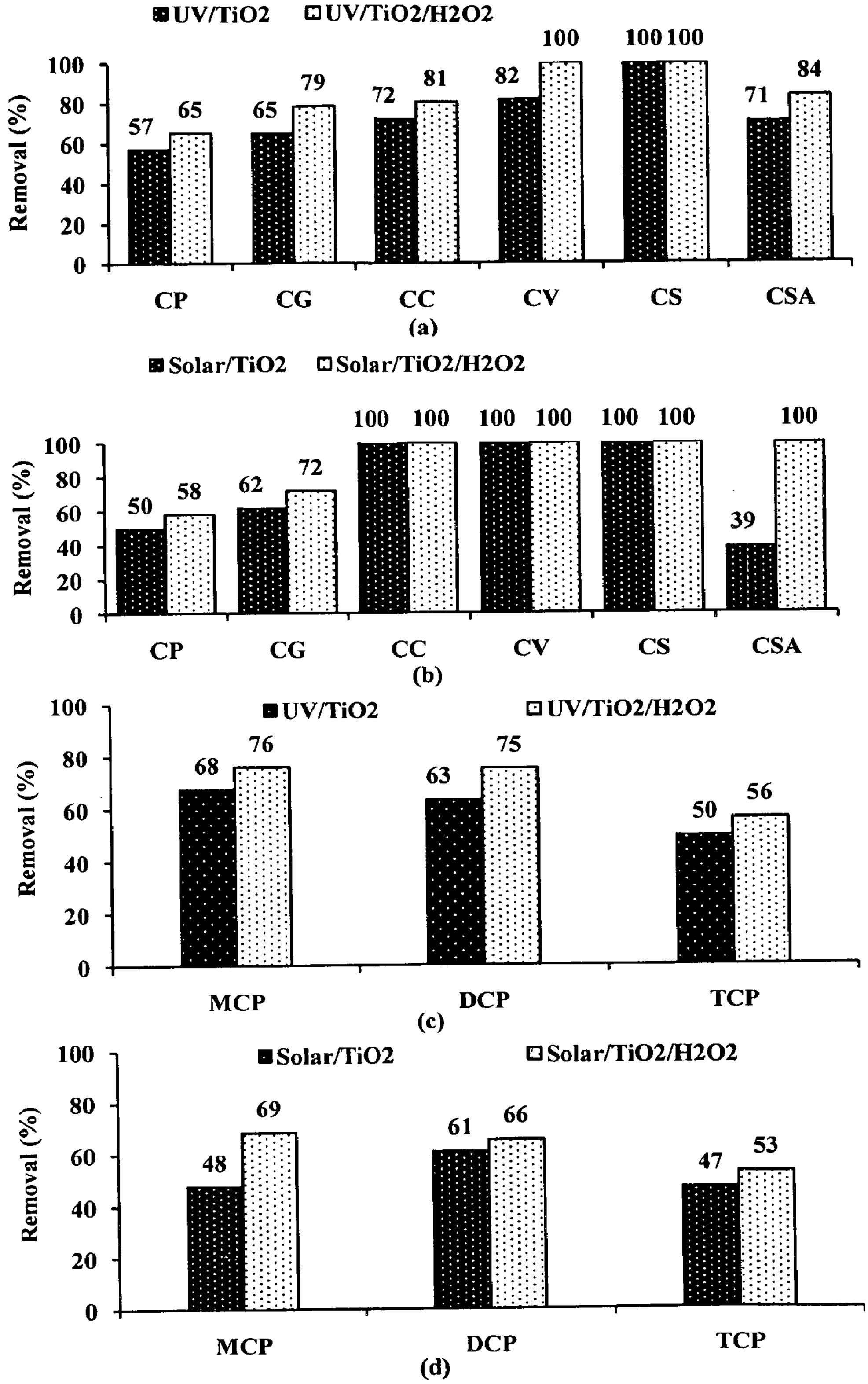


Figure 4.21 Comparison of different treatment processes for the removal (%) of chlorophenolics by chemical family (a and b) and number of attached chlorine atoms (c and d) for PC effluent of Mill A

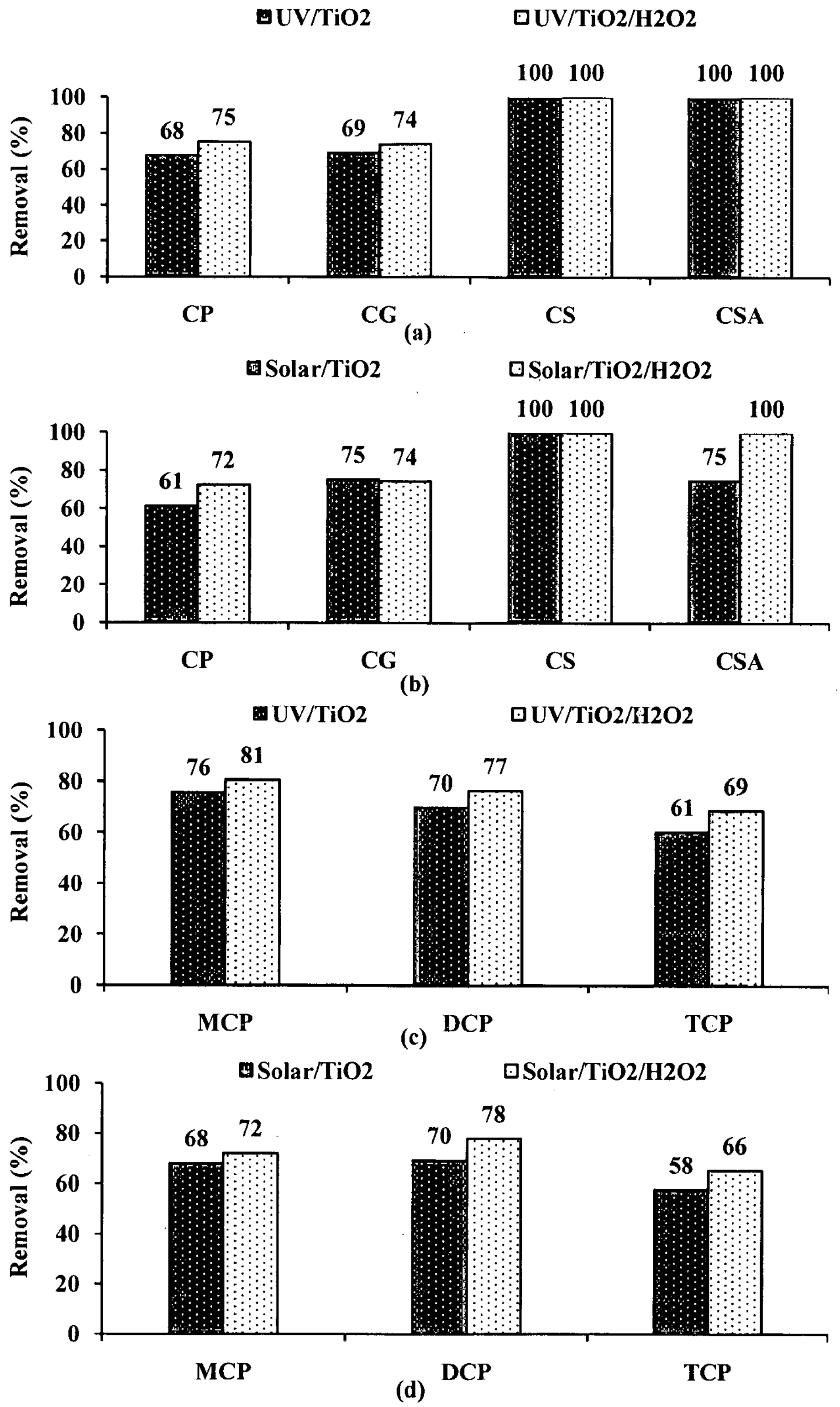


Figure 4.22 Comparison of different treatment processes for the removal (%) of chlorophenolics by chemical family (a and b) and number of attached chlorine atoms (c and d) for BT effluent of Mill A

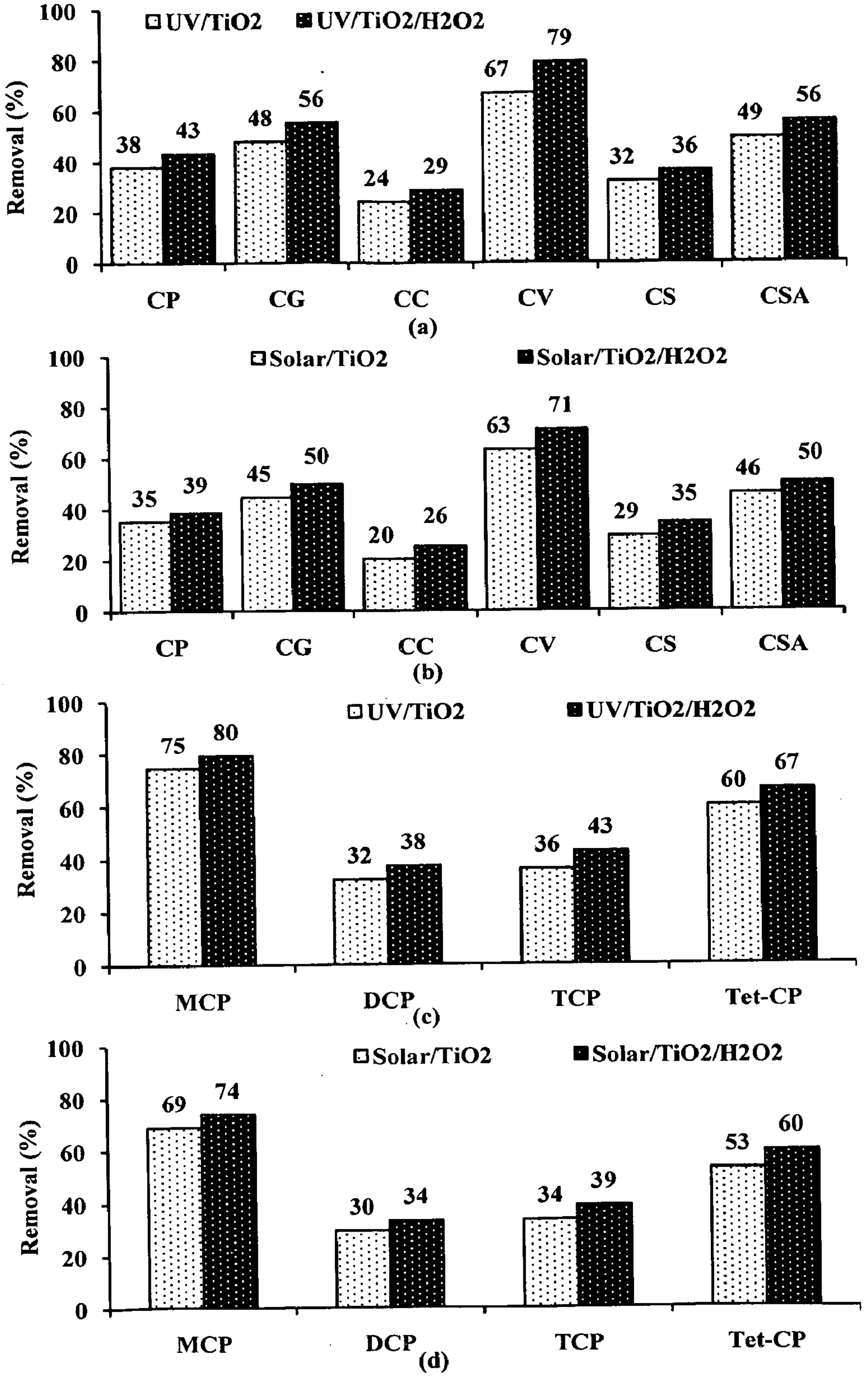


Figure 4.23 Comparison of different treatment processes for the removal (%) of chlorophenolics by chemical family (a and b) and number of attached chlorine atoms (c and d) for PC effluent of Mill B

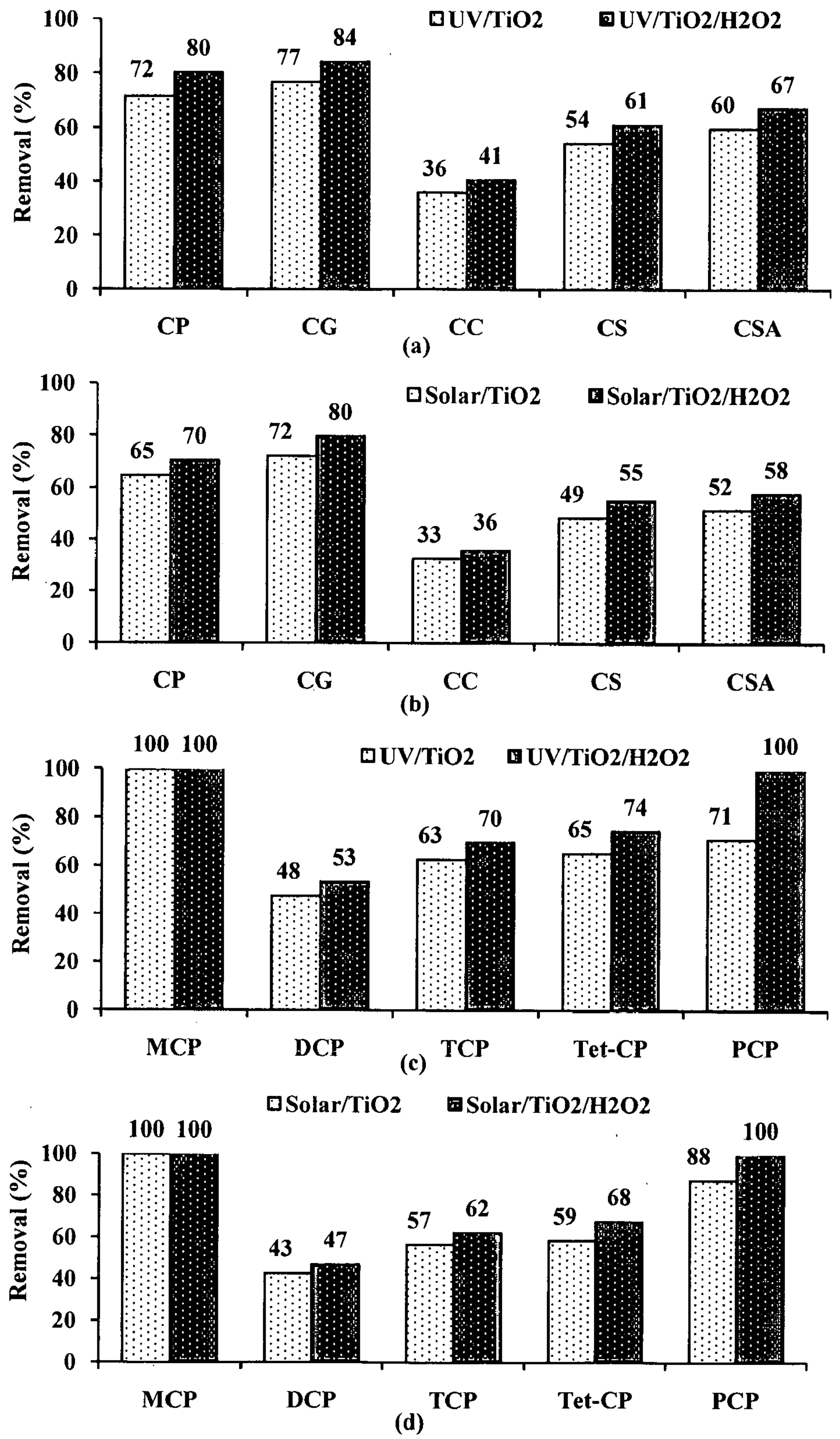


Figure 4.24 Comparison of different treatment processes for the removal (%) of chlorophenolics by chemical family (a and b) and number of attached chlorine atoms (c and d) for BT effluent of Mill B

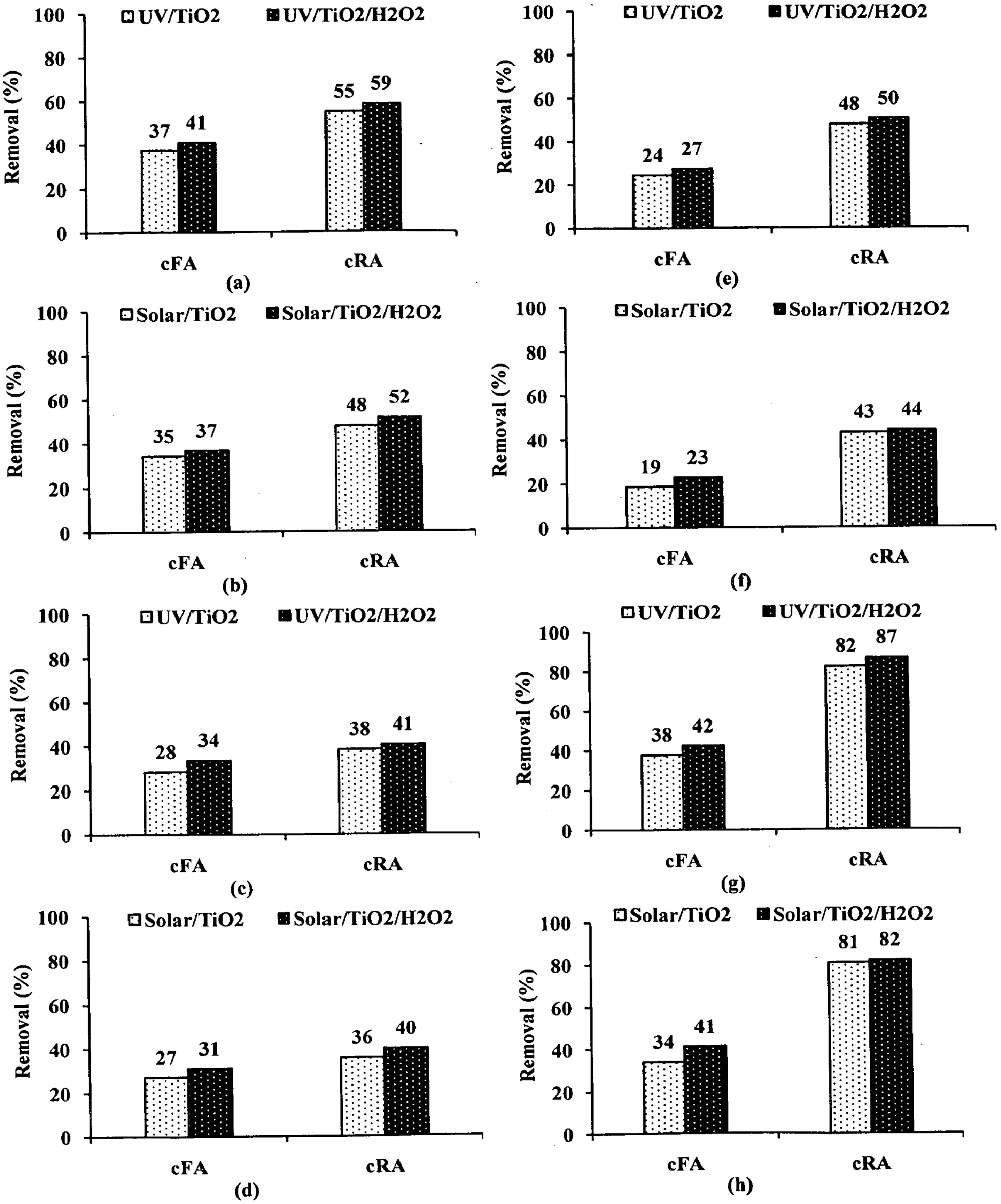


Figure 4.25 Comparison of different treatment processes for the removal (%) of cRA and cFA from effluents of Mill A: PC (a-b), BT (c-d) and Mill B: PC (e-f), BT (g-h)

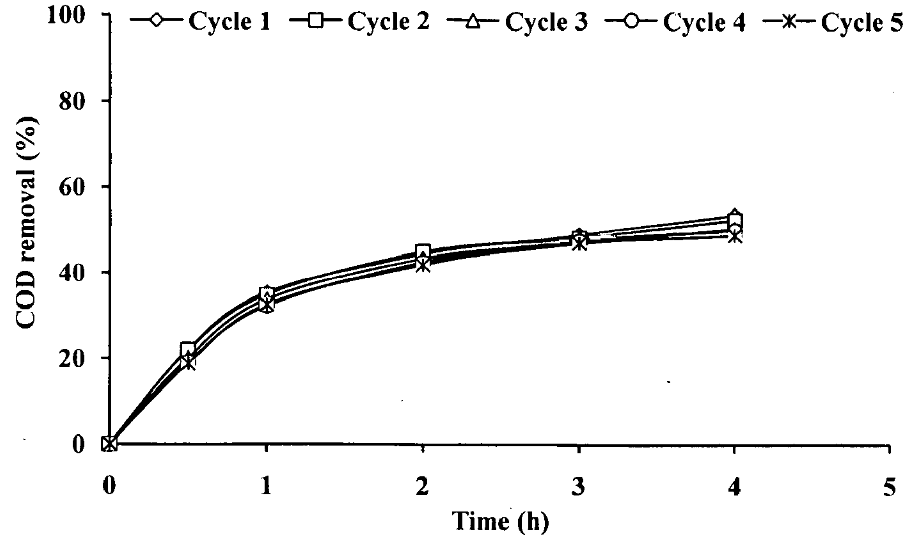


Figure 4.26 Effect of catalyst recycling on COD removal efficiency for PC effluent after five cycles of treatment with UV/TiO$_2$ process

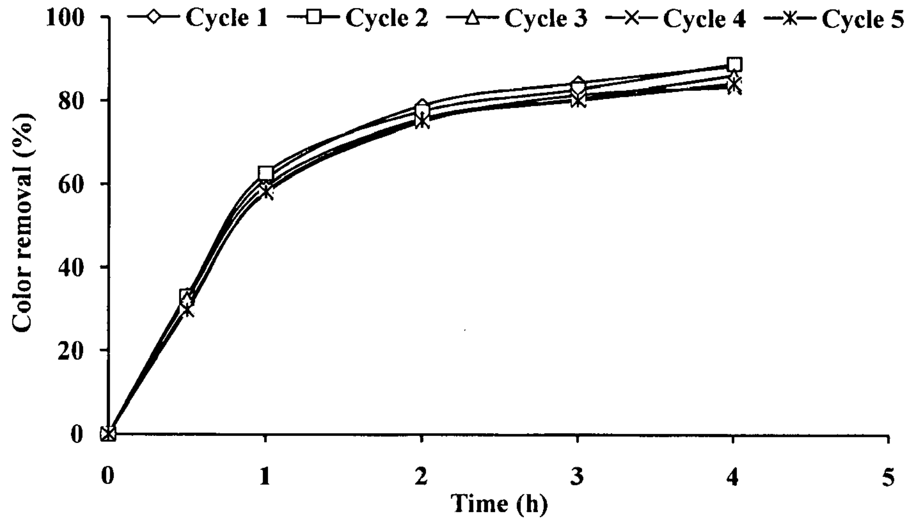


Figure 4.27 Effect of catalyst recycling on color removal efficiency for PC effluent after five cycles of treatment with UV/TiO$_2$ process

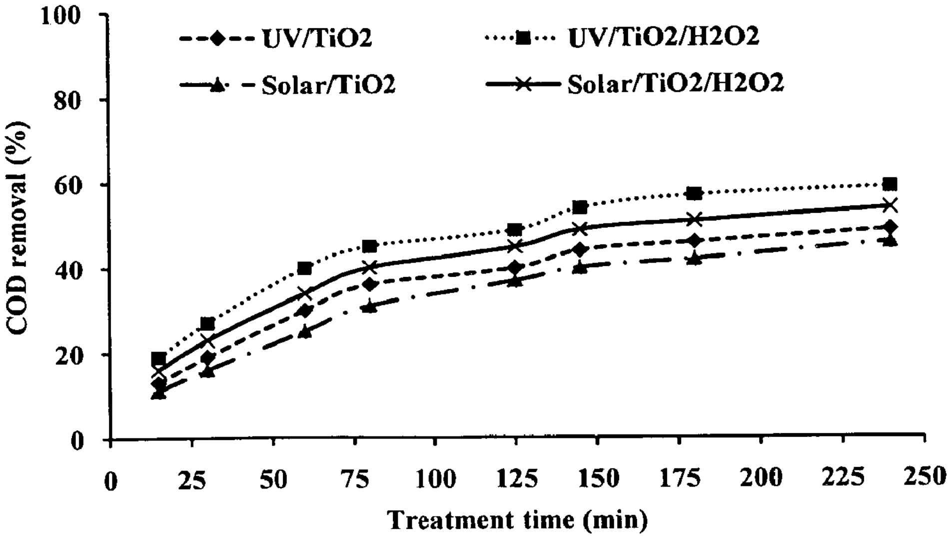


Figure 4.28 COD removal (%) from PC effluent by UV/TiO_2, UV/TiO_2/H_2O_2, Solar/TiO_2, and Solar/TiO_2/H_2O_2 processes with treatment time

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CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

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5.1 CONCLUSIONS

Based on the present study, the following conclusions can be drawn:

1. Solar/TiO_2/H_2O_2 process was found economical, environment friendly, and suitable for the remediation of pulp and paper mill effluents. Photocatalysis was found less effective for the removal of chloro-resin and fatty acids.
2. The photocatalysis improved biodegradability of the effluents by removal of toxic compounds. This indicates the easy removal of the degradation products in the biotreatment.
3. The catalyst can be reused without significant loss in pollutants removal efficiency thereby leading to reduced treatment cost.
4. TCP were generated in higher proportion during D/CED sequence as compared to other sequences. This lead to higher toxicity of the effluents from this sequence. PCP is not generated during DE$_P$D and ODED sequences. CP were the major compounds generated during D/CED where as CG were the major compounds generated during other sequences.

5.2 RECOMMENDATIONS AND FUTURE WORK

1. Solar/TiO_2/H_2O_2 process appears to be a better option for large scale industrial effluent treatment.
2. The photocatalysis as a pre-treatment step to biological treatment is good to improve the biodegradability of the pollutants for their further degradation by the biological processes.
3. Further pilot plant investigations are needed to confirm the benefits observed in the laboratory studies.

4. The catalyst development for high photo-efficiency, wider pH range application, catalyst immobilization to avoid separation, and reduction of the oxidant addition needs further research.
5. The photocatalysis integration with other processes for enhanced photo-mineralization and development of effective photocatalytic reactor design for higher utilization of solar energy is needed.
6. The paper mills targeting the reduction of generation of chloroorganics and AOX may consider ODED and DE$_P$D sequences over D/CED sequence.