Chlorophenolics Oxidation from Pulp Bleaching Effluents Using Photocatalysis

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ABSTRACT:
The chlorophenolics oxidation from the pulp bleaching effluents of DE_PD sequence (D_1 and E_P stage) using TiO_2 photocatalysis has been investigated. The BOD/COD ratio of the effluents was low, i.e. 0.26 and 0.25 for D_1 and E_P stage effluents, respectively, indicating low biodegradability of the organics. The photocatalytic oxidation experiments were carried out with UV radiation under optimized conditions (TiO_2 = 0.50 g/L, H_2O_2 = 15 mM/L, pH = 7.0, and reaction time = 4 h), in a slurry reactor. 64 and 61% removal of chlorophenolics was achieved for D_1 and E_P stage effluents, respectively, with UV/TiO_2/H_2O_2 process which is higher as compared to UV/TiO_2 process. H_2O_2 addition to the photocatalytic system improved chlorophenolics degradation efficiency. Chlorophenols (CP) were removed to the maximum extent (92%) followed by chlorocatechols (CC) (73%) and chloroguaiacols (CG) (57%) for D_1 stage effluent while for E_P stage effluent, CC were not detected after treatment, chlorosyringaldehyde (CSA) was removed up to 86% followed by chlorovanillin (CV) (78%), CP (74%), and CG (57%) with UV/TiO_2/H_2O_2 process. 2,6-dichlorophenol (2,6-DCP), 4,6-dichloroguaiacol (4,6-DCG), and 3,4,5-trichloroguaiacol (3,4,5-TCG) from D_1 stage effluent and 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 4,5,6-trichloroguaiacol (4,5,6-TCG), and tetrachlorocatechol (TetCC) from E_P stage effluent were not detected after treatment with UV/TiO_2/H_2O_2 process. While, UV/TiO_2 process resulted in the complete removal of 4,6-dichloroguaiacol (4,6-DCG) and 4,5,6-trichloroguaiacol (4,5,6-TCG) from D_1 and E_P stage effluents, respectively. UV/TiO_2/H_2O_2 process was found to be an attractive technique for the oxidation of chlorophenolics from the pulp bleaching effluents as compared to UV/TiO_2 process.

1. INTRODUCTION

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 (Dence and Reeve, 1996). The pulp bleaching is used to achieve the desirable pulp brightness. The bleaching with Cl_2 and chlorine derived chemicals is known to generate various chloroorganics (> 500) in the effluent, i.e. phenolics, chloro-resin and fatty acids, dioxins and furans etc., which are collectively, estimated as adsorbable organic halides (AOX) (Roy et al., 2004). The chloroorganics generation is directly proportional to the consumption of the bleach chemicals (Savant et al., 2006).

Chloroorganics are toxins, biorecalcitrant, and tend to persist in nature, hence are known as persistent organic pollutants (USEPA, 1998). They can be segregated in high molecular weight (HMW >1000 Dalton) and low molecular weight (LMW <1000 Dalton) fractions as defined by ultra filtration (Duarte et al., 2003). 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. 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 bio-accumulate through food chain and are potentially toxic (Mittal and Maheshwari, 2001).

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 (Sawant and Ranade, 2002).

The use of elemental chlorine free (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 (Ali and Sreekrishnan, 2001). H_2O_2 application in the alkaline extraction (E_P) stage increases delignification and pulp brightness while decreases active chlorine requirement in the subsequent bleaching stages, cost, and the effluent pollution load (Leporini Filho et al., 2003). The conventional biological process utilized by Indian paper industry for effluent treatment suffers from low efficiency for chlorinated organics removal and no color decrease (Lindstrom and Mohamed, 1988). The photocatalysis is an emerging technique for the remediation of both aquatic and atmospheric pollutants (Fujishima et al., 1999). 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 the 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 (Carp et al., 2004).

TiO_2 photocatalysis has been successfully utilized for the treatment of pulp and paper industry effluents. Mansilla et al. (1997) 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. Perez et al. (2001) reported that photocatalysis is efficient for the removal of AOX, total organic carbon (TOC), total phenols, and toxicity from ECF bleaching effluent. The aim of this work is to characterize the chlorophenolics generated during bleaching of mixed hardwood kraft pulp using DE_PD sequence and their subsequent removal by effluent treatment with UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes.

2. EXPERIMENTAL

2.1. Materials

Titanium dioxide (TiO_2) and hydrogen peroxide (30% H_2O_2) (High Media, SQ grade) were used as photocatalyst and oxidant, respectively, for the photocatalytic oxidation experiments and the latter was also used for alkaline extraction (E_P stage) of pulp. TiO_2 is predominantly anatase (99.97 wt. %, X-ray diffraction, Bruker AXS D8) with a mean surface area of 26.11 m^2/g (N_2 adsorption, Micromeritics, Chemi Soft TPx V1.02) and average particle size of 50-150 nm (field emission scanning electron microscopy, FEI Quanta 200 F). The various isomers of chlorophenols (CP), used as reference compounds, were received from Aldrich, USA. Chlorocatechols (CC), chloroguaiacols (CG), chlorovanillin (CV), chlorosyringaldehyde (CSA), and chlorosyringol (CS), were obtained from Helix Biotech. Corporation (Richmand, BC Canada). All the standards were of the highest purity commercially available. HPLC grade *n*-hexane, acetone, and LR grade diethyl ether were used as solvents. Analytical grade acetic anhydride was used after double distillation. Other reagents and chemicals used were of analytical grade. The stock standard solutions of chlorophenolics (20-30 mg/L) were prepared in the acetone/water (10:90). The pH of the pulp and the effluents was adjusted with 1M H_2SO_4 or NaOH solutions. Sodium chlorite ($NaClO_2$) solution was used for in-situ generation of chlorine dioxide in D stage. NaOH solution was used for the alkaline extraction of pulp in E_P stage. The unbleached mixed hardwood (Eucalyptus : Poplar, 70 : 30) kraft pulp was procured from a pulp and paper mill. The pulp was hand washed with plenty of water, screened, air dried, and stored in the air tight polythene bags.

2.2. Pulp Bleaching

For generating effluent, the pulp was bleached to a target brightness of 87% ISO using $D_1E_PD_2$ sequence under the controlled laboratory conditions (Table 1). D and E_P refer to chlorine dioxide and peroxide reinforced alkaline extraction stages, respectively. The chlorine demand on the pulp was calculated using the following equation:

$$Chlorine\ demand\ (\%) = kappa\ no. \times kappa\ factor \quad (1)$$

Table 1. Pulp Bleaching Conditions

Parameters	D_1 Stage	E_P Stage
Kappa no.	15	
Kappa factor	0.3	
aCl^- applied (% demand)	70	----
NaOH (% O.D. pulp)	----	0.7
Consistency (%)	10	10
pH (end)	3.5	10.5
Temperature (ºC)	70	70
Time (min)	180	90
H_2O_2 (% O.D. pulp)	----	0.3

All chemicals charged as %O.D. (oven dried) pulp basis.

Of the total chemical charge, 70% was given in D_1 stage and remaining 30% in D_2 stage. All the bleaching experiments were performed in polythene bags with 200 g O.D. unbleached pulp. The disintegrated pulp was adjusted to desired consistency and pH. The bleaching chemicals were added to the pulp, hand mixed, and placed in a water bath at desired temperature. The pulp was well kneaded by hand mixing 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 used for characterization and photocatalytic oxidation.

2.3. Effluent Treatment

The photocatalytic oxidation experiments were carried out in a timber-framed UV reactor equipped with 4 UV tubes (18 W each) in completely mixed and batch mode at ambient conditions. The detailed configuration of the reactor is described elsewhere (Kumar et al., 2011a). The effluent (500 mL) was adjusted to pH 7.0 and 0.5 g/L of TiO_2 added. The reaction mixture was magnetically stirred in the dark for 30 minutes prior to adding H_2O_2 (15 mM/L) and switching on UV lamps, to make sure the adsorption/desorption equilibrium. 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. The supernatant was collected and used for analysis. The removal of chlorophenolics after photocatalytic oxidation was quantified according to the following equation:

$$Removal\ (\%) = [(C_0 - C)/ C_0] \times 100 \quad (2)$$

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

The improvement in biochemical oxygen demand (BOD)/ chemical oxygen demand (COD) ratio of the effluents was also investigated to assess the biodegradability of the pollutants. All the experiments were performed in duplicate and the average values have been reported.

2.4. Analytical Methods

The effluents were characterized in terms of BOD, COD, and color (UV-VIS spectrophotometer - SPEKOL 2000, Analytic Jena) according to the Standard Methods (Clesceri et al., 1998). A bench scale pH meter (TOSHNIWAL) was used to measure the pH. AOX was analysed on AOX analyser (ECS 1200, THERMO). The chlorophenolics were analysed on Gas Chromatograph (GC) – Mass Spectrometer (MS) (Trace GC - Ultra-DSQ, Thermo Electron Corporation). The chlorophenolics were extracted from the effluents and derivatized according to the standard procedure (Lindstrom and Nordin, 1976; Abrahamsson and Xie, 1983). 1.0 µL of the chlorophenolics acetyle derivative was injected into the GC column. 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 of 38-45 mTorr. All injections were made in the splitless (1 min) mode. The target compounds in the effluent were first identified by matching their mass spectrum with the NIST library. Once main peaks were identified,

pure standard solutions of target compounds were injected into the GC-MS system for determining retention time (RT). The quantitative analysis was performed with the help of calibration curve and extraction efficiency determination of individual chlorophenolics (Kumar et al., 2011b).

3. RESULTS AND DISCUSSION

3.1. Effluent Characteristics

The average analytical characteristics of pulp bleaching effluents are summarized in Table 2 and 3. D_1 stage effluent is characterized with higher COD load as compared to E_P stage. While E_P stage effluent is characterized with high color as compared to D_1 stage. The BOD/COD ratio of the effluents is low indicating low biodegradability of the organics present in the effluents. GC - MS facilitated identification and quantization of various LMW chlorophenolic compounds with high degree of chlorination i.e. chlorophenols (CP), chloroguaiacols (CG), chlorocatechols (CC), chlorovanillin (CV), and chlorosyringaldehyde (CSA). Eighteen chlorophenolic compounds were detected. Similar chloroorganics have been reported to be present in the pulp bleaching effluents by other authors (Roy et al., 2004). The corresponding retention time (RT), base peak mass/charge (m/z) ratio, concentration, and extraction efficiency (EE) are mentioned in Table 3.

3.2. Photocatalytic Oxidation

The presence of chlorinated organics (AOX) and low BOD/COD ratio renders the effluents unsuitable for biological degradation because they may affect development of microorganisms and thus efficiency of biological oxidation. Hence, the advanced oxidation of pulp bleaching effluents with TiO_2 photocatalysis has been investigated for removal of bio-refractory organics. The first two bleaching stages (D_1 and E_P) are the major source of pollution load in the effluent. Hence we focused our study to the oxidation of pollutants from the effluents of only these stages. For the successful catalysis, the initial COD of the effluent should be below 800 mg/L because high quantity of organic matter tends to cover the catalyst surface through adsorption and causes scattering of light radiation (Gogate and Pandit, 2004). Hence, the effluents were diluted to bring the initial COD value to 500 mg/L before photocatalysis. The photocatalytic oxidation has been investigated under optimized conditions (TiO_2 = 0.50 g/L, H_2O_2 = 15 mM/L, pH 7.0, and reaction time = 4 h) using UV/TiO_2 and UV/TiO_2/H_2O_2 processes.

After 4 h of irradiation, UV/TiO_2/H_2O_2 process removed chlorophenolics up to 64% which is higher as compared to UV/TiO_2 process (57%) for D_1 stage effluent (Table 3). With UV/TiO_2 process, CP were removed to the maximum extent (87%) followed by CC (66%) and CG (50%) (Fig. 1). 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 the 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%) (Fig. 2). While UV/TiO_2/H_2O_2 process removed CP to the maximum extent (92%) followed by CC (73%) and CG (57%) (Fig. 1). 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 to 54%. 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%) (Fig. 2).

While for E_P stage effluent, UV/TiO_2/H_2O_2 process removed chlorophenolics up to 61% which is higher as compared to UV/TiO_2 process (53%) (Table 3). UV/TiO_2 process removed CC to the maximum extent (90%) followed by CSA (83%), CV (74%), CP (68%), and CG (49%) (Fig. 3). 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%) (Fig. 4). While UV/TiO_2/H_2O_2 process resulted in complete degradation of CC. CSA was removed up to 86% followed by CV (78%), CP (74%), and CG (57%) (Fig. 3). 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%) (Fig. 4).

Table 2. Average Analytical Characteristics of the Pulp Bleaching Effluents

Parameter	D_1 Stage	E_P Stage
COD (mg/L)	813	673
BOD (mg/L)	212	168
BOD/COD ratio	0.26	0.25
Color (mg Pt-Co/L)	980	1113
pH	3.3	10.5
AOX (mg/L)	18	15.3

Table 3. RT, m/z, EE, Concentration and Removal (%) of Chlorophenolics for D_1 and E_P Stage Effluents

Chlorophenolics	**RT (min)**	**m/z**	**EE (%)**	**Ci (µg/L)**		**Removal (%)**			
						UV/TiO_2		**UV/TiO_2/H_2O_2**	
				D_1	**E_P**	**D_1**	**E_P**	**D_1**	**E_P**
3-chlorophenol (3-CP)	14.20	127.9	49	0.11	1.35	92	56	97	64
4-chlorophenol (4-CP)	14.36	127.9	98	0.04	0.02	81	87	96	ND
2,6-dichlorophenol (2,6-DCP)	16.52	161.9	64	0.04	ND	86	-----	ND	-----
2,5-dichlorophenol (2,5-DCP)	16.96	161.9	106	0.13	0.61	93	89	89	92
2,4-dichlorophenol (2,4-DCP)	16.98	161.8	87	0.01	0.02	84	92	91	ND
3,4-dichlorophenol (3,4-DCP)	18.27	161.9	81	0.04	0.04	77	75	79	81
4-chloroguaiacol (4-CG)	18.70	157.9	104	1.56	4.39	58	52	65	59
2,4,5-trichlorophenol (2,4,5-TCP)	19.07	195.8	77	0.09	0.07	86	87	93	97
4,5-dichloroguaiacol (4,5-DCG)	21.19	191.9	79	4.12	6.00	47	46	54	55
2,3,4-trichlorophenol (2,3,4-TCP)	21.23	195.8	63	0.06	0.06	79	84	93	95
4,6-dichloroguaiacol (4,6-DCG)	22.27	191.9	102	0.03	0.06	ND	90	ND	95
3,6-dichlorocatechol (3,6-DCC)	22.50	177.9	3	2.14	ND	59	-----	66	-----
3,5-dichlorocatechol (3,5-DCC)	22.77	177.9	5	0.62	ND	83	-----	91	-----
3,4,5-trichloroguaiacol (3,4,5-TCG)	24.40	225.8	99	0.01	ND	82	-----	ND	-----
4,5,6-trichloroguaiacol (4,5,6-TCG)	25.07	225.9	100	ND	0.05	-----	ND	-----	ND
5,6-dichlorovanillin (5,6-DCV)	25.85	219.9	73	ND	0.06	-----	74	-----	78
Tetrachlorocatechol (Tet-CC)	28.31	247.8	33	0.25	0.18	83	90	88	ND
2,6-dichlorosyringaldehyde (2,6-DCSA)	28.59	249.9	75	ND	0.22	-----	83	-----	86
Total				**9.3**	**13.1**	**57**	**53**	**64**	**61**

ND - not detected, Ci – initial concentration

The photocatalytic oxidation of organic pollutants occurs by the concomitant action of highly reactive intermediate species, i.e. hydroxyl radicals ($OH^{\bullet}$), holes (h^{+}), superoxide radicals ($O^{\bullet -}_{2ads}$), and hydroperoxyl radicals ($OOH^{\bullet}$) (Sleiman et al., 2007). H_2O_2 addition improved the rate of photocatalytic degradation of chloroorganics. This is due to production of additional $OH^{\bullet}$ radicals by its decomposition and reaction with superoxide radical anion. Furthermore, it also accepts conduction band e^{-}_{cb} and thus prevents e^{-}_{cb}/h^{+}_{vb} re-combination. The biodegradability of the pollutants present in the effluents was estimated in terms of improvement in the BOD/COD ratio after photocatalysis. For the complete biodegradation, the effluent must have a BOD/COD ratio of at least 0.4 (Chamarro et al., 2001). The BOD/COD ratio improved to 0.34 and 0.41 for D_1 stage and 0.33 and 0.38 for E_P stage effluents after treatment with UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes, respectively. The partial mineralization of the organic pollutants leading to the structural changes is responsible for the improvement in the BOD/COD ratio (Yeber et al., 2000). For D_1 stage effluent, BOD/COD ratio increased over the optimal value (0.4) after treatment with $UV/TiO_2/H_2O_2$ process. These findings show easy removal of the pollutants by the biological treatment. The difference observed in the photooxidation efficiency of chlorophenolics may be due to the difference in the number and position of chlorine atoms on the aromatic ring, electronic nature, adsorption over the catalyst surface, concentration and intermediates formed.

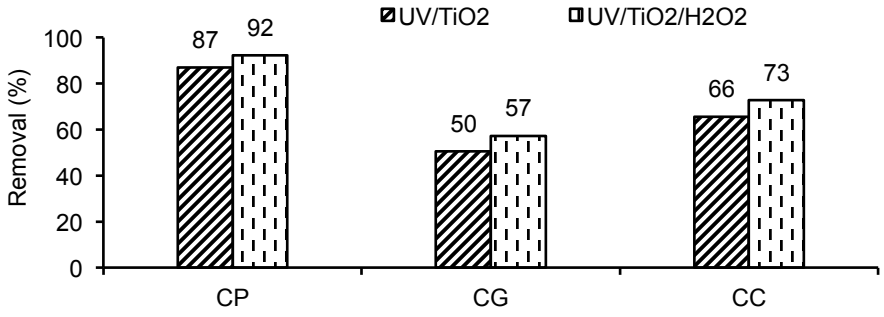

Figure 1. Removal (%) of chlorophenolics by chemical family for D_1 stage effluent

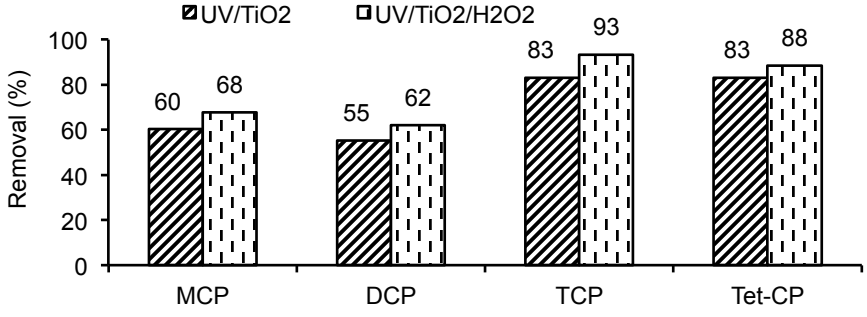

Figure 2. Removal (%) of chlorophenolics by number of attached chlorine atoms for D_1 stage effluent

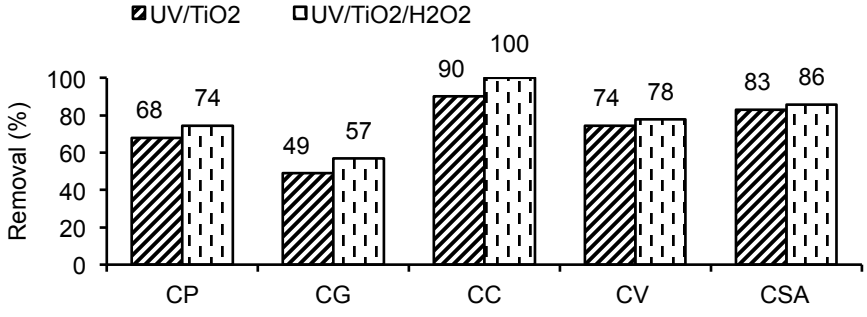

Figure 3. Removal (%) of chlorophenolics by chemical family for E_P stage effluent

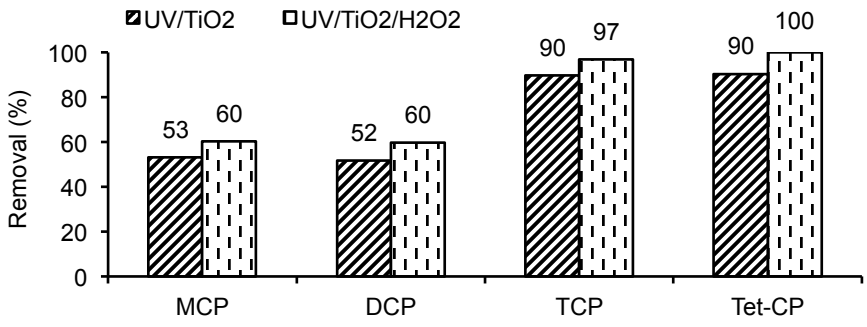

Figure 4. Removal (%) of chlorophenolics by number of attached chlorine atoms for E_P stage effluent

CONCLUSION

The experimental findings show that TiO_2 photocatalysis is an attractive technique for the oxidation of chlorophenolics from pulp bleaching effluents. Higher pollutants removal efficiency was achieved with $UV/TiO_2/H_2O_2$ process as compared with UV/TiO_2. The biodegradability index of the effluents improved after photocatalytic oxidation with both the processes. This indicates easy removal of the degradation products during biological treatment. The photocatalysis, using solar light as an economical light source, may be a potential technology in future for remediation of biorecalcitrant pollutants.

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