Color Removal From Kraft Pulp Bleaching Wastewater Using Heterogeneous Photocatalysis

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ABSTRACT

The decolorization of the kraft pulp bleaching wastewater (D/CED, D_1ED_2, $D_1E_PD_2$ and OD_1ED_2 bleaching sequences) with UV/TiO_2 and $UV/TiO_2/H_2O_2$ advanced oxidation processes has been studied. The photocatalytic-oxidation experiments were performed under UV radiation in a slurry-type reactor at a pH 7.0 with TiO_2 (0.5 g/L) as a catalyst and H_2O_2 (15 mM/L) as an oxidant. Both the treatment processes were found efficient for the decolorization of the wastewater. The photodegradation efficiency improved with the addition of H_2O_2 (15 mM/L) to the UV/TiO_2 process. Promising results i.e. 95.3 % and 76.4 % color removal for D/C and E stages of D/CED, 90.9 % and 88.5 % color removal for D_1 and E stages of D_1ED_2, 92.4 % and 90.4 % color removal for D_1 and E_P stages of $D_1E_PD_2$, and 98.4 % and 97.3 % color removal for D_1 and E stages of OD_1ED_2 bleaching sequences, respectively, were obtained after 4 h of treatment with $UV/TiO_2/H_2O_2$ process. The higher color reduction was obtained with $UV/TiO_2/H_2O_2$ process compared to UV/TiO_2 process. The highest color removal efficiency was obtained for OD_1ED_2 bleaching sequence wastewaters. The D_1 or D/C bleaching stage wastewaters were more amenable to the photocatalytic degradation as compared to the E or E_P stage.

KEYWORDS: Photocatalytic oxidation; bleaching wastewater; UV/TiO_2; $UV/TiO_2/H_2O_2$; kraft pulp; decolorization.

Introduction

The pulp and paper sector comes under twelve most polluting industries in India due to the huge quantity and quality of wastewater generated [1]. Among the various sections, the wastewaters from pulp bleaching are responsible for most of the color, organic matter and toxicity of the water discharges of this industry [2]. The paper mill discharges are characterized to be highly dark brown colored. First two stages of hardwood/ softwood pulp bleaching typically contribute over 90 % of the total bleach plant wastewater color and the E stage individually, 70-80 % [3]. The color in the wastewater originates from the thermal, mechanical, and chemical conversion of wood into pulp. During these operations, the cellulose and hemicelluloses are separated from the lignin and other extractives in the wood. These operations generate residual lignin and lignin derivatives, along with polymerized tannins in the paper mill wastewater as by-products of lignin degradation, which are responsible for wastewater color [4].

The color contributes negatively to the

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aesthetic value and affects the biological productivity of water body by inhibiting the process of photosynthesis due to reduced light penetration [1]. The color depletes dissolved oxygen levels in water by increasing water temperature due to the absorption of infrared radiation. The color is also associated with wood extractives and chlorinated organics (e.g. phenols, dioxins and furans), formed during pulp bleaching, which are organic toxins and persistent in the environment [4]. The discharge of these hazardous compounds to the environment can affect the ecological balance.

The conventional wastewater treatment processes i.e. physical and biological treatment systems, which are effective for the reduction of BOD (Biochemical Oxygen Demand), high molecular weight chloro-lignins, and TSS (Total Suspended Solids) in the wastewater are not suitable for the complete removal of small molecular weight chloro-organics and color [5]. Hence, there is an urgent need to adopt some advanced treatment methods i.e. advanced oxidation processes (AOP's) for meeting increasingly stringent wastewater discharge standards.

The heterogeneous photocatalysis, an AOP, is an important procedure for wastewater treatment, which can cause

the complete mineralization of a wide range of organics without any harmful environmental impact [6-7]. Photocatalysis is based on the generation of very reactive oxidizing species i.e. OH radicals. When a photon of light ($\lambda < 390$ nm) strikes the catalyst surface, an electron (e^-) is raised from the valence band to the conduction band leaving behind a hole (h^+). The h^+ can either directly oxidize a wide range of adsorbed pollutants or produce OH radicals (from H_2O/OH^- ion) which can also oxidize organics non-selectively. The e^- is readily taken by adsorbed O_2 to produce superoxide ion (O_2^-), thus preventing the electron-hole re-combination. The O_2^- radical can further participate in contaminant degradation reactions [8].

TiO_2 as a photocatalyst has been successfully utilized for the remediation of pulp and paper mill wastewaters during the recent years. Perez *et al* [9] reported that photocatalysis can efficiently reduce the organic load from the ECF (Elemental Chlorine Free) bleaching wastewater. About 80 % AOX (Adsorbable Organic Halides), 64 % COD (Chemical Oxygen Demand), and 72 % color removal was achieved with $UV/TiO_2/O_2$. Pedroza *et al* [10] investigated that sequential, biological

and photocatalytic treatment resulted in about complete degradation of bleaching wastewater in terms of COD (97 %), color (92 %), and chlorophenols (99 %). Yeber *et al* [11] used Cu (II) as an electron acceptor for the photocatalytic oxidation. About 94 % color, 70 % COD, and 50 % TOC (Total Organic Carbon) removal was reported. Thus, TiO_2 photocatalysis is potentially suited for the remediation of color and chloro-organics from pulp and paper mill bleaching wastewater.

The present study is aimed to study the photocatalytic decolorization of kraft pulp bleaching wastewater (D/CED, D_1ED_2, $D_1E_PD_2$ and OD_1ED_2 bleaching sequences) with UV/TiO_2 and $UV/TiO_2/H_2O_2$ advanced oxidation processes.

Experimental Methodology

1. Materials

Unbleached mixed hardwood kraft pulp was procured from a paper mill in India. The pulp was washed with water, air dried, and stored in polythene bags for further bleaching experiments. TiO_2 and analytical grade H_2O_2 (30 %) were obtained from Fisher Scientific (SQ grade). Other reagents and chemicals used were of analytical grade. 1M H_2SO_4 or 1M NaOH solutions were used for adjusting the pH of the pulp and aqueous solutions. Sodium chlorite ($NaClO_2$) solution was used for in-situ generation of chlorine dioxide. The chlorine bleach liquor for D/C stage was also procured from the paper mill. NaOH solution was used for alkaline extraction of the pulp.

1. Bleaching procedure

The pulp was bleached to 87 % ISO target brightness with the D/CED, D_1ED_2, $D_1E_PD_2$ and OD_1ED_2 sequences, where D/C, D_1, D_2, E, E_P, and O refer to chlorination using 50 % substitution by

chlorine dioxide, first chlorine dioxide, second chlorine dioxide, alkaline extraction, peroxide enforced alkaline extraction, and oxygen delignification stages, respectively. The experimental conditions for different pulp bleaching stages are listed in Table 1. Pulp disintegration was done at 3 % consistency for 5 min before any treatment for bleaching. Oxygen pre-bleaching was performed with NaOH solution and $MgSO_4$ in the laboratory autoclaves revolving in hot ethylene glycol bath.

After the oxygen delignification pulp was washed with water, air dried, and stored in polythene bags for further studies. The oxygen delignification was targeted to a kappa number drop between 40-50 %. The total chlorine charge on the pulp was calculated from the following formula:

Chlorine demand (%)
= kappa no. × kappa factor

Polythene bags were used for all bleaching stages, except D/C stage which was performed in a closed plastic container. The bleaching was performed with 200 g O.D. pulp in two

sets (100 + 100 g). The disintegrated pulp was adjusted to desired consistency and pH. Bleach liquor was added to the pulp; hand mixed and kept in water bath at desired temperature. The pulp was kneaded from time to time during bleaching. After bleaching, the pulp (100 g O.D.) was washed with 900 ml of distilled water in three stages in a Buchner funnel. The filtrate and washings of both set (each 100 g O.D.) were mixed and stored in refrigerator at 4 ^{0}C for further characterization and photocatalytic oxidation studies.

2. Photocatalytic system

The photocatalytic degradation of wastewater was performed in a borosilicate glass bowl (1L), placed in a timber-framed UV reactor (77 cm × 36 cm × 71 cm). 4 UV lamps (= 365 nm), each of 18 W (Philips) fitted on the top side of the reactor and 15 cm away from the sample, were used as radiation source (Fig. 1). The wastewater was subjected to irradiation with continuous stirring. The heat generated by the UV lamps was lowered by using a fan fitted on the side wall of the reactor.
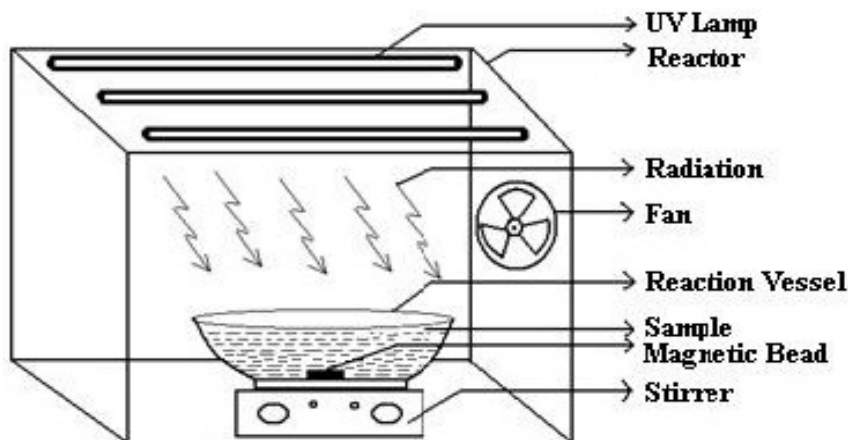

Fig. 1: Photocatalytic reactor used for wastewater advanced oxidation

Table 1: Experimental conditions for various bleaching stages

Parameters	D/CED			D_1ED_2			$D_1E_PD_2$			OD_1ED_2			
	D_{50}/C_{50}	E	D	D_1	E	D_2	D_1	E_P	D_2	O	D_1	E	D_2
Kappa no.	15			15			15			8.3			
Kappa factor	0.30			0.35			0.30			0.30			
Cl_2 (% demand)	70 (50:50)	----	30	70	----	30	70	----	30	----	70	----	30
NaOH (% O.D. pulp)	----	1	----	----	0.7	----	----	0.7	----	2	----	0.7	----
H_2O_2 (%O.D. pulp)	----	----	----	----	----	----	----	0.3	----	----	----	----	----
Consistency (%)	3	10	10	10	10	10	10	10	10	10	10	10	10
End pH	2	10.5	3.5	3.4	11.5	3.5	3.5	10.5	3.3	----	3.5	11.4	3.2
Temperature (°C)	Ambient	70	70	70	70	70	70	70	70	100	70	70	70
Time (min)	45	90	180	180	90	180	180	90	180	75	180	90	180
O_2 Charge (kg/cm²)	----	----	----	----	----	----	----	----	----	6	----	----	----
$MgSO_4$ (%)	----	----	----	----	----	----	----	----	----	0.2	----	----	----
Brightness (% ISO)	87			87			87			87			

3. Photocatalytic oxidation

500 ml bleaching wastewater, adjusted to pH 7.0, was taken in the glass bowl and 0.5 g/L of TiO_2 was added. The reaction mixture was stirred for 30 minutes before adding peroxide (15 mM/L) and turning on the UV lamps. The experiments were performed for 4 hours in a completely mixed and batch mode at ambient temperature and cooling was not provided. After photocatalytic oxidation, water loss was made up by distilled water and TiO_2 was allowed to settle overnight in refrigerator below 4 ^{0}C. The

supernatant was collected and TiO_2 agglomerates were removed by centrifuging before characterization.

4. Methods of analysis

The pulp was characterized according to the standard procedures: pulp kappa number - Tappi T 236, chemical pulps disintegration SCAN C 18 : 65, pulp brightness ISO Standard 2469, indicators and standard solutions preparation T 610 om-87. COD was estimated by closed reflux titrimetric method and BOD by measuring dissolved oxygen before and after incubation at $20\,^{0}C$ for 5 day. The color measurement was done at 465 nm by using a UV-VIS double beam spectrophotometer (SPEKOL 2000, Analytic Jena) [12]. The pH was measured by using a bench scale pH meter (TOSHNIWAL). Iodometric method was used for the analysis of residual H_2O_2 [13]. The wastewater decolorization rate was quantified according to the following formula: \
Degradation (%) = [$(C_0\ C)/C_0$] × 100

Where:

   C_0 = initial concentration

   C = concentration after photo-degradation

All the experiments were performed in duplicate and the average values are reported.

Results and discussion

The bleaching wastewaters characteristics utilized for the photo-degradation experiments are summarized in the Table 2. The first two bleaching stages (D/C or D_1 and E or E_P) are the major source of environmental pollution load in terms of BOD, COD, and color. Hence, we focused our study only to the wastewater decolorization of these bleaching stages with UV/TiO_2 and $UV/TiO_2/H_2O_2$ advanced oxidation processes.

The initial COD load of the wastewater should be below 800 mg/L for successful photocatalysis because excess of the organics cause scattering of light and saturate the catalyst surface

by adsorption [14]. Hence, D_1 (D_1ED_2 and $D_1E_PD_2$) and E/E_P (D/CED, D_1ED_2, and $D_1E_PD_2$) stage bleaching wastewaters were diluted to bring the initial COD load to approximately 500 mg/L before photodegradation experiments. The optimum photocatalytic degradation conditions for pulp and paper mill wastewater were investigated in the laboratory. 0.5 g/L of TiO_2, 15 mM/L of H_2O_2, pH 7.0, and 4 h of reaction time was found to be optimum for the degradation of the organic matter from the paper mill wastewater. The D/C or D_1 and E or E_P stage wastewaters of D/CED, D_1ED_2, $D_1E_PD_2$ and OD_1ED_2 bleaching sequences were subjected to photocatalytic degradation under these optimized conditions.
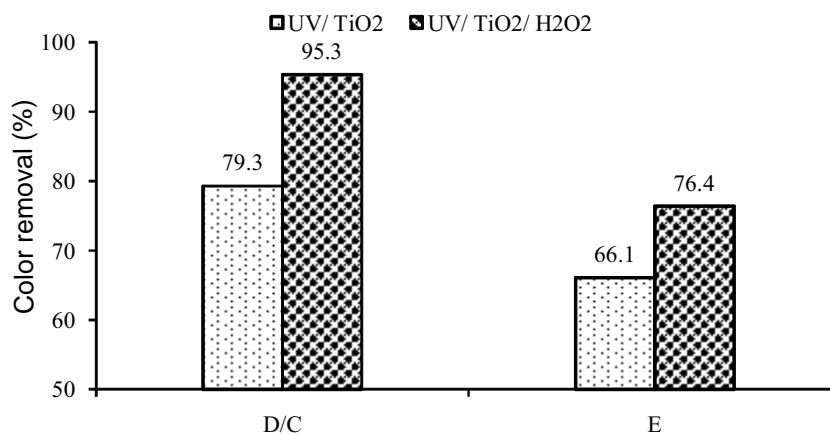
1. Decolorization of D/CED bleaching wastewaters

Fig. 2 depicts the decolorization efficiency of UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes for D/C and E stage wastewaters of D/CED bleaching sequence. 95.3 % and 76.4 % color removal was achieved for D/C and E stage wastewaters, respectively, with $UV/TiO_2/H_2O_2$ process. These values

were higher compared to the values obtained with UV/TiO_2 process. Addition of peroxide to the UV/TiO_2

increased the decolorization efficiency. H_2O_2 increases the decolorization efficiency because it can additionally absorb light radiation and directly form $OH^.$ radicals. It can also accept the conduction band electrons to generate $OH^.$ radicals, thus prevent e^-/h^+ recombination and increases the life of valence band holes [15]. Higher decolorization efficiency was obtained for D/C stage wastewater as compared to E stage. This may be due to already low color of D/C stage wastewater and difference in the nature and concentration of organics [16].

2. Decolorization of D_1ED_2 bleaching wastewaters

Fig. 3 represents the decolorization efficiency of UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes for D_1 and E stage wastewaters of D_1ED_2 bleaching sequence. 90.9 % and 88.5 % color removal was achieved for D_1 and E stage wastewaters, respectively, with $UV/TiO_2/H_2O_2$ process. This color removal was higher compared to the color removal with UV/TiO_2 process. Similar decolorization trend was also observed here i.e. higher for D_1 stage wastewaters as compared to E stage. Higher color removal was obtained for

E stage wastewater of D_1ED_2 bleaching sequence as compared to D/CED with $UV/TiO_2/H_2O_2$ process. As the replacement of molecular chlorine by chlorine dioxide in the bleaching process increases, the amount of color generated in the wastewater decreases [17]. Hence, the color of E stage wastewater of D_1ED_2 bleaching sequence was already low as compared to D/CED, so higher decolorization rates were observed.

Table 2:
Average bleaching wastewater characteristics used for photocatalysis

Parameters	D/CED		D_1ED_2		$D_1E_PD_2$		OD_1ED_2	
	D_{50}/C_{50}	E	D_1	E	D_1	E_P	D_1	E
COD (mg/L)	371.1	780	1053.3	853.3	813.3	673.3	430.8	340.1
BOD (mg/L)	77.9	148.2	253.3	204.8	211.5	168.3	120.6	98.6
Color (mg Pt-Co/L)	352.6	1886.7	1040.0	1226.7	980.3	1113.3	121.8	133.3
pH	1.9	10.5	3.4	11.5	3.3	10.5	3.5	11.4
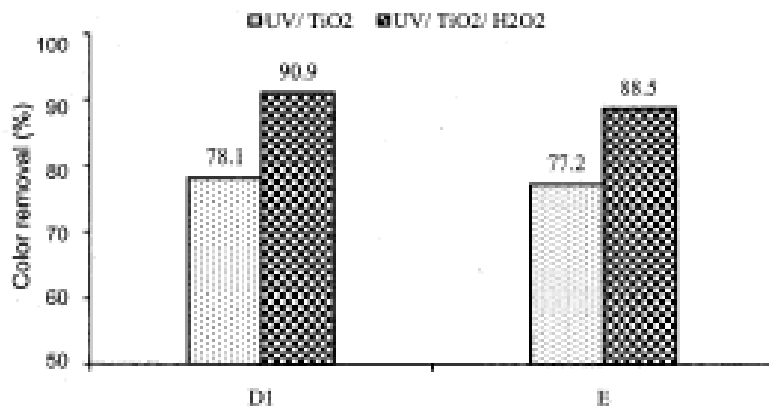
Fig. 3: Decolorization of D_1 and E stage wastewaters of D_1ED_2 bleaching sequence with UV/TiO_2 and $UV/TiO_2/H_2O_2$.
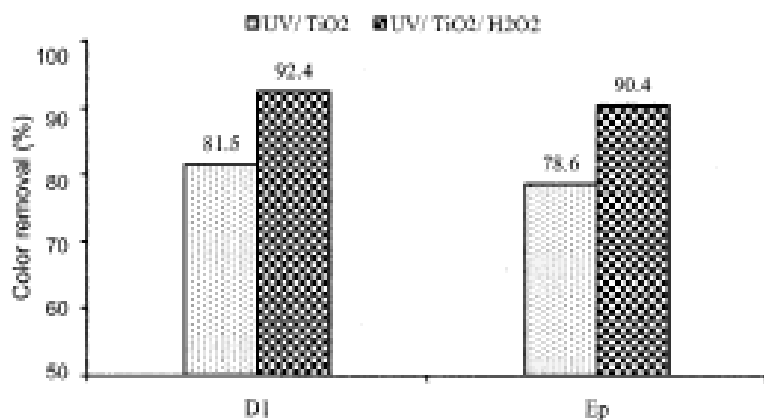
Fig. 4: Decolorization of D_1 and E_p stage wastewaters of $D_1E_pD_1$ bleaching sequence with UV/TiO_2 and $UV/TiO_2/H_2O_2$.

Fig. 5: Decolorization of D_1 and E stage wastewaters of OD_1ED_2 bleaching sequence with UV/TiO_2 and $UV/TiO_2/H_2O_2$.

3. Decolorization of $D_1E_PD_2$ bleaching wastewaters

Fig. 4 depicts the decolorization efficiency of UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes for D_1 and E_P stage wastewaters of $D_1E_PD_2$ bleaching sequence. 92.4 % and 90.4 % color removal was achieved for D_1 and

E_P stage wastewaters, respectively, with $UV/TiO_2/H_2O_2$ process. This color removal is higher compared to the color removal obtained with UV/TiO_2 process. For $D_1E_PD_2$ bleaching sequence wastewaters, higher decolorization efficiency was achieved as compared to D_1ED_2. A lower

decolorization efficiency was obtained for D_1 stage wastewater as compared to D/C stage of D/CED bleaching sequence. For E_P stage wastewater higher color removal was obtained as compared to E stage of D/CED and D_1ED_2 bleaching sequences. This is due to the use of peroxide as an oxidant in the alkaline extraction stage which reduces the molecular chlorine multiple required in the first bleaching stage which in turn decreases the formation of color, chlorinated dioxins, furans, phenols, and AOX in the wastewater [18]. Due to this, the color of E stage wastewater of $D_1E_PD_2$ bleaching sequence was already low as compared to D/CED and D_1ED_2, hence higher decolorization efficiency was obtained.

4. Decolorization of OD_1ED_2 bleaching wastewaters

Fig. 5 depicts the decolorization efficiency of UV/TiO_2 and $UV/TiO_2/H_2O_2$ processes for D_1 and E stage wastewaters of OD_1ED_2 bleaching sequence. 98.4 % and 97.3 % color removal was achieved for D_1 and E stage wastewaters, respectively, with $UV/TiO_2/H_2O_2$ process. This color removal is higher compared to the color removal obtained with UV/TiO_2 process. The highest decolorization efficiency was obtained for OD_1ED_2 bleaching wastewaters. This is due to the reduction (44.7%) of initial kappa number (i.e. residual lignin) of the pulp in the OD_1ED_2 bleaching sequence after oxygen predelignification stage, which in turn reduces the active chlorine multiple required for the next bleaching stages and thus environmental load [18]. According to literature, oxygen prebleaching decreases the color of bleaching effluents by 63-80% [19]. Thus, the color of OD_1ED_2 bleaching wastewaters was already very low as compared to D/CED, D_1ED_2, and $D_1E_PD_2$ sequences. Hence, higher decolorization efficiency was obtained. The difference in the color removal efficiency for wastewaters of different bleaching sequences may also be due to the difference in the molecular weights and structure of the dissolved organic pollutants present in the effluents and organic load [16].

Conclusion

$UV/TiO_2/H_2O_2$ and UV/TiO_2 advanced oxidation processes were found to be

highly efficient for the decolorization of kraft pulp bleaching wastewaters. OD_1ED_2 bleaching wastewaters were decolorized to the highest extent as compared to D/CED, D_1ED_2, $D_1E_pD_2$ sequences. Addition of 15 mM/L of peroxide to the UV/TiO_2 process accelerated the photocatalytic decolorization efficiency. Promising results i.e. 95.3 % and 76.4 % color removal for D/C and E stages of D/CED, 90.9 % and 88.5 % color removal for D_1 and E stages of D_1ED_2, 92.4 % and 90.4 % color removal for D_1 and E_p stages of $D_1E_pD_2$, and 98.4 % and 97.3 % color removal for D_1 and E stages of OD_1ED_2 bleaching sequences, respectively, were obtained after 4 h of treatment with $UV/TiO_2/H_2O_2$ process. $UV/TiO_2/H_2O_2$ process was found to be more effective for the wastewater decolorization as compared to UV/TiO_2. The D_1 or D/C bleaching stage wastewaters were more easily decolorized by the photocatalytic treatment as compared to the E or E_p stage.

Acknowledgements

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