2011 International Conference on Environmental and Agriculture Engineering
IPCBEE vol.15(2011) © (2011) IACSIT Press, Singapore

Advanced Oxidation of Pulp and Paper Industry Effluent

Parveen Kumar, Satish Kumar, Nishi K. Bhardwaj [+] and Ashutosh Kumar Choudhary

Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur, U. P., India

Abstract. The advanced photocatalytic oxidation of the pulp and paper industry effluent (primary clarified and biotreated) has been studied with UV/TiO_2 and UV/TiO_2/H_2O_2 treatment processes for environmental load reduction. The photo-oxidation experiments are performed under UV radiation in a slurry-type of reactor with optimized treatment conditions i.e. pH 7.0, 0.5 g/L of TiO_2 and 15 mM/L of H_2O_2 for 4 hours. The BOD (Biochemical Oxygen Demand)/ COD (Chemical Oxygen Demand) ratio of the effluents is low i.e. 0.25 and 0.12 for primary clarified and biotreated effluents, respectively, indicating that biorefractory organics are present. Addition of hydrogen peroxide to the UV/TiO_2 system enhances the photoprocess performance. The treatment for 4 hrs with UV/TiO_2/H_2O_2 removes the organic load of the primary clarified effluent by 57.9 % in COD, 42.9 % in BOD, and 89.2 % in color and of biotreated effluent by 74.8 % in COD, 52.7 % in BOD, and 95.4 % in color, which is higher as compared to UV/TiO_2 process. Higher COD, BOD, and color reduction is obtained for biotreated effluent as compared to primary clarified one. The BOD/COD ratio of the effluents improved after photocatalytic oxidation, i.e. 0.09 and 0.11 points for biotreated effluent and 0.06 and 0.09 points for primary clarified effluent with UV/TiO_2 and UV/TiO_2/H_2O_2 treatment processes, respectively.

Keywords: Advanced oxidation, paper mill effluent, biodegradability, UV/TiO_2, UV/TiO_2/H_2O_2.

1. Introduction

The pulp and paper industry effluents contain a variety of toxic organic compounds that may cause deleterious environmental impacts to receiving water bodies if discharged untreated. Among the various sections, the effluents from pulp bleaching are responsible for most of the color, organic matter, and toxicity of the water discharges of this industry [1]. The pulp produced by chemical pulping requires bleaching to produce bright pulps. The use of chlorine gas and chlorine compounds as bleaching chemicals is known to generate various toxic and bio-refractory chlorinated organics (phenols, resin and fatty acids, dioxins and furans) in the paper mill effluent [2]. Some of them are toxic, mutagenic, and resistant to biodegradation. The conventional effluent treatment processes are not effective for their complete degradation. Hence, treatment with some advanced oxidation processes (AOP's) is needed [3].

TiO_2 photocatalysis, an AOP, is an important alternative because it can cause the complete mineralization of a wide range of organics without any harmful environmental impact [4]. When a photon of light strikes the catalyst surface, an electron is raised from the valence band to the conduction band leaving behind a hole (h^+_{vb}), eqn. (1) [1]. h^+_{vb} can either directly oxidize a wide range of adsorbed pollutants or by producing $OH^\bullet$ radicals (from H_2O/OH^- ion), eqn. (2 and 3), which can also oxidize organics non-selectively, eqn. (7). Electron (e^-_{cb}) is readily taken by adsorbed O_2 to produce superoxide ion ($O_2^{\bullet-}$), eqn. (4), thus prevents the electron-hole recombination. $O_2^{\bullet-}$ can further participate in contaminants degradation reactions [5]. Addition of H_2O_2 to the photocatalytic system increases the degradation efficiency positively because it can additionally form $OH^\bullet$ radicals either by direct radiation absorption or by accepting conduction band electrons, eqn. (5 and 6) [6].

[+] Corresponding author. Tel.: +91-132-2714350; fax: +91-132-2714311.
E-mail address: nishifpt@iitr.ernet.in.

$$TiO_2 + hv \rightarrow e_{cb}^- + h_{vb}^+ \quad (1)$$

$$h_{vb}^+ + H_2O_{ads} \rightarrow OH_{ads}^\bullet + H^+ \quad (2)$$

$$h_{vb}^+ + OH_{ads}^- \rightarrow OH_{ads}^\bullet \quad (3)$$

$$e_{cb}^- + O_{2ads} \rightarrow O_{2ads}^{\bullet -} \quad (4)$$

$$H_2O_2 + hv \rightarrow OH^\bullet + OH^\bullet \quad (5)$$

$$H_2O_2 + e_{cb}^- \rightarrow OH^\bullet + OH^- \quad (6)$$

$$OH^\bullet + Conta\min ants \rightarrow Intermidiates \rightarrow CO_2 + H_2O + endproducts \quad (7)$$

TiO_2 photocatalysis has been efficiently utilized for the remediation of pulp and paper mill effluents during the recent years. Perez *et al.* [7] investigated that photocatalysis is efficient for the reduction of AOX (Adsorbable Organic Halides) (95 %), TOC (Total Organic Carbon) (50 %), total phenols, and toxicity from the bleaching effluent. Boyd and Almquist [8] found out that photocatalysis with TiO_2 is an effective method for the degradation of COD (Chemical Oxygen Demand) and toxicity from pulp and paper mill effluents. The present work is aimed to study the advanced oxidation of pulp and paper industry effluent (primary clarified and biotreated) with UV/TiO_2 and UV/TiO_2/H_2O_2 treatment processes for environmental load reduction.

2. Materials and Methods

2.1 Materials

Titanium dioxide (SQ grade) and analytical grade H_2O_2 (30 %) were obtained from Fisher Scientific. Other reagents and chemicals used were of analytical grade and used without any further purification. The pH of the aqueous solutions was adjusted with 1M H_2SO_4 or 1M NaOH solutions. Combined effluents from pulping, pulp bleaching, and paper making (primary clarified and biotreated) were procured from a paper mill in India and stored in refrigerator below 4 ^{0}C temperature before use. The factory uses mixed hardwood as raw material.

2.2 Advanced oxidation

The photo-oxidation experiments were carried out in a timber-framed UV (Ultra Violet) reactor (77 cm × 36 cm × 71 cm) equipped with 4 UV tubes (λ = 365 nm) each of 18 W (Philips) on the top side 15 cm away from the sample [9]. 500 mL paper mill effluent was adjusted to pH 7 and transferred to a borosilicate glass bowl. 0.5 g/L of TiO_2 was added and the aqueous suspension was magnetically stirred for 30 minutes before adding H_2O_2 (15 mM/L) and switching on the UV lamps. One fan fitted on the side wall was used to lower the heat generated by UV lamps. All the experiments were carried out in completely mixed and batch mode at ambient conditions. After completion of the reaction, water loss was made up by distilled water and kept for settling overnight in refrigerator below 4 ^{0}C temperature. Supernatant was collected and TiO_2 agglomerates were removed by centrifuging before analysis. The rate of degradation was followed in terms of the percent removal in COD, BOD (Biochemical Oxygen Demand), and color after photocatalytic treatment, eqn. (8). The change in biodegradability index (BOD/COD) of the effluents was also investigated for assessing the biodegradability of treated effluents.

$$Degradation(\%) = [(C_0 - C)/C_0] \times 100 \quad (8)$$

Where, C_0 and C are the concentration of pollutants before and after photo-oxidation, respectively.

2.3 Analytical methods

The effluent was characterized before and after photocatalysis according to the Standard Methods [10]. COD was determined by closed reflux titrimetric method and BOD by measuring dissolved oxygen before and after incubation at 20 ^{0}C for 5 days. The color was measured at 465 nm using UV-VIS double beam spectrophotometer (SPEKOL 2000, Analytic Jena). A bench scale pH meter (TOSHNIWAL) was used to measure the pH. The effluent after treatment was analysed for residual H_2O_2 by the iodometric method [11]. All the experiments were performed in duplicate and average values reported.

3. Results and Discussion

The average bleaching effluents characteristics utilized for the present study are summarized in the table 1. The primary clarified effluent presented high organic load in terms of BOD, COD, and color. The biological treatment is inefficient for the removal of color and complete degradation of chlorinated organics. Hence, there is a need for advanced chemical oxidation of these effluents. According to literature the initial COD of the effluent should be below 800 mg/L for the successful photocatalysis because excess of the organic matter tends to recover the catalyst surface through adsorption and causes scattering of light radiation [12]. Hence, we diluted primary clarified effluent to bring the initial COD values around 500 mg/L before photocatalysis while biotreated effluent was used directly. After preliminary studies the optimum treatment conditions for photocatalytic degradation of pulp and paper mill effluent were searched out i.e. pH 7.0, TiO_2 0.5 g/L, H_2O_2 15 mM/L and reaction time of 4 hrs [9]. The primary clarified and biotreated paper mill effluents were subjected to photocatalytic degradation under these optimized conditions. The effluents were prequilibrated with TiO_2 for 30 min before illumination and addition of peroxide. About 9.7 % and 9.9 % COD removal for primary clarified and biotreated effluents, respectively, was observed prior to photocatalytic oxidation. This may be due to the initial dark adsorption of organic matter on the catalyst surface [13]. The adsorption of pollutants on the catalyst surface is important because the photogenerated holes on the catalyst surface can either directly oxidize the pollutants or by generating hydroxyl radicals [5].

Table 1: Average analytical characteristics of the pulp and paper mill effluents.

S. No.	Parameters	Primary clarified effluent	Biotreated effluent
1.	COD (mg/L)	1092±4	246±2
2.	BOD (mg/L)	274±3	29±1
3.	BOD/COD ratio	0.25	0.12
4.	Color (mg Pt-Co/L)	2066±4	1012±2
5.	pH	7.5±0.4	7.4±0.2

Chemical oxygen demand (COD), an important measure of water pollution, is necessary to be monitored during the photocatalytic degradation of a pulp bleaching effluent. Hence degradation of organic matter present in the effluents was monitored in terms of percent COD removal. After 4 hrs of treatment for primary clarified effluent, 46.8 % and 57.9 % COD removal and for biotreated effluent 64.6 % and 74.8 % COD removal with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes, respectively, was obtained as shown in the fig. 2. A higher COD removal efficiency was obtained for the biotreated effluent as compared to the primary clarified effluent. The biological treatment process may convert some functional groups of organic pollutants to more easily oxidisable forms that are then easily degraded during photocatalysis, hence higher COD removal efficiency was obtained [14]. The difference in the COD removal efficiency for different effluents may be due to the difference in the structure, molecular weight of the dissolved organic pollutants present in the effluents and organic load [15]. $UV/TiO_2/H_2O_2$ treatment system was found to be more efficient for the COD degradation for both the effluents than UV/TiO_2.

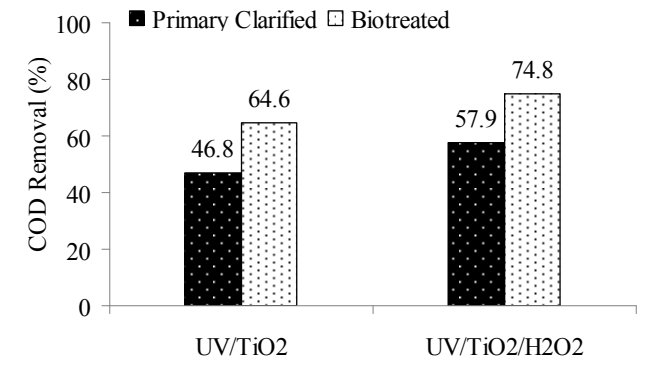

Fig. 2: COD removal (%) from primary clarified and biotreated paper mill effluents.

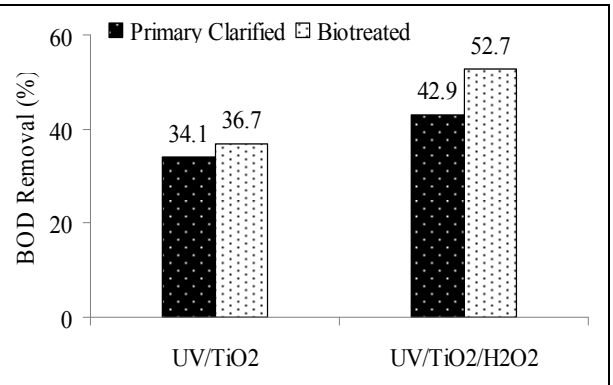

Fig. 3: BOD removal (%) from primary clarified and biotreated paper mill effluents.

Biochemical oxygen demand (BOD) of all the effluents was determined before and after the photocatalytic treatment. After 4 hrs of treatment for primary clarified effluent 34.1 % and 42.9 % BOD removal and for biotreated effluent 36.7 % and 52.7 % BOD removal with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes, respectively, was obtained as shown in the fig. 3. A significant removal of BOD was observed for both the effluents, probably due to the photochemical degradation of the biodegradable species and low toxicity of the effluents [16]. The biodegradability of the pollutants present in the effluents was estimated in terms of the BOD/COD ratio. The initial biodegradability index of the effluents was low i.e. 0.25 and 0.12 for primary clarified and biotreated effluents, respectively, indicating that biorefractory organics are present. For complete biodegradation, the effluent must present a biodegradation index of at least 0.40 [17]. As can be seen in the fig. 4 and 5, moderate improvement in biodegradability index (BOD/COD) has been observed, the values being 0.09 and 0.11 points for biotreated effluent and 0.06 and 0.09 points for primary clarified effluent with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment systems, respectively. Yeber *et al.* [18] also reported moderate increase in the biodegradability of ECF bleaching effluents with heterogeneous systems. For biotreated effluent increase in BOD/COD ratio was higher as compared to primary clarified effluent which is in accordance with the literature [14].

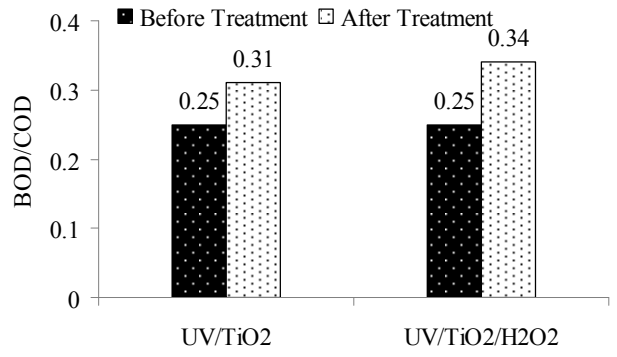

Fig. 4: Changes in the BOD/COD ratio of primary clarified paper mill effluent.

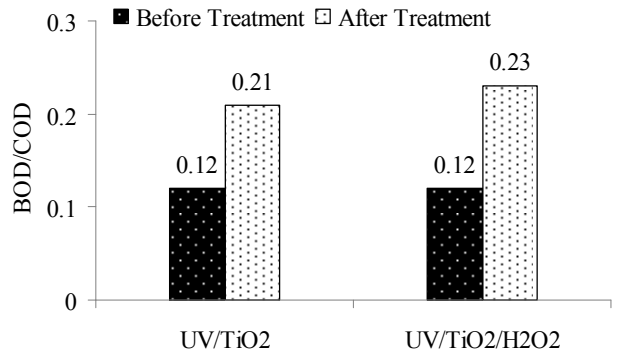

Fig. 5: Changes in the BOD/COD ratio of biotreated paper mill effluent.

The brown color in the pulp and paper mill effluents is primarily due to the presence of lignin and it's derivatives (high molecular weight substances which contributes 60 % to 80 % of color) that are released from the substrate during bleaching [19]. Fig. 6 depicts the color removal efficiency of titanium dioxide photocatalysis for primary clarified and biotreated effluents. Color of biotreated effluent was already low as compared to primary clarified effluent. Hence for biotreated effluent higher color removal was observed i.e. 79.4 % and 95.4 % as compared to primary clarified i.e. 75.3 % and 89.2 % with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes, respectively. Heterogeneous photocatalysis has been reported to be more efficient for the discoloration of effluents, reaching 40 % color removal within first minute of treatment. The major effect of heterogeneous systems was reaction acceleration [20]. Balcioglu and Arslan [14] also observed that titanium dioxide photocatalysis removed color from biologically pretreated effluent more effectively than for untreated effluent.

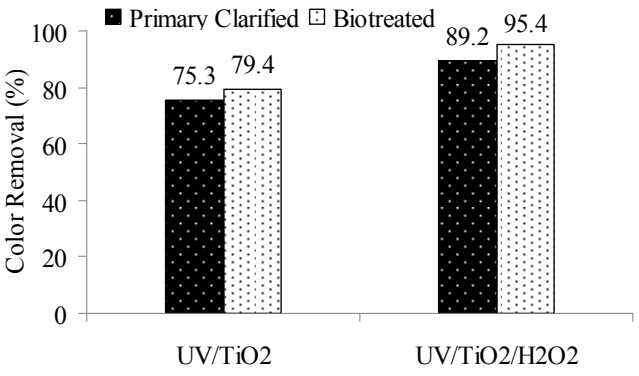

Fig. 6: Color removal (%) from primary clarified and biotreated paper mill effluents.

4. Conclusion

Addition of hydrogen peroxide (15 mM/L) to the UV/TiO_2 treatment system enhanced the photoprocess performance. 4 hrs of treatment with UV/TiO_2/H_2O_2 removed the organic load of the primary clarified effluent by 57.9 % in COD, 42.9 % in BOD, and 89.2 % in color and of biotreated effluent by 74.8 % in COD, 52.7 % in BOD, and 95.4 % in color, which is higher as compared to UV/TiO_2 system. Higher COD, BOD and color reduction is obtained for biotreated effluent as compared to primary clarified one. Both the treatment processes increase the biodegradability of the effluents moderately and improve water quality. UV/TiO_2/H_2O_2 treatment system was found more efficient for the remediation of pulp and paper mill effluents as compared to UV/TiO_2. The experiments utilising solar radiation for the photocatalytic degradation of pulp and paper mill effluent are in progress.

5. Acknowledgements

The research grant for this study provided by Ministry of Human Resource and Development, Government of India is gratefully acknowledged.

6. References

[1] S. K. Kansal, M. Singh and D. Sud. Wastewater quality at kraft / soda agro-based paper mills and its treatment using a heterogeneous photocatalytic system. *Desalination* 2008, **228**: 183-190.

[2] M. Roy, S. K. Chakrabarti, N. K. Bhardwaj, S. Chandra, S. Kumar, S. Singh and P. K. Bajpai. Characterization of chlorinated organic material in Eucalyptus pulp bleaching effluents. *J. Sci. Indus. Res.* 2004, **63**: 527-535.

[3] E. C. Catalkaya and F. Kargi. Advanced oxidation treatment of pulp mill effluent for TOC and toxicity removal. *J. Env. Manag.* 2008, **87**: 396-404.

[4] S. Ahmed, M. G. Rasul, W. N. Martens, R. Brown and M. A. Hashib. Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments. Desalination 2010, **261(1-2)**: 3-18.

[5] R. A. Al-Rasheed. Water treatment by heterogeneous photocatalysis an overview. *Proc. of the 4th SWCC Acquired Experience Symposium*: Jeddah, 2005. Online: http://www.swcc.gov.sa/files/assets/Research/TechnicalPapers/Chemstry/WATERTREATMENTBYHETEROGENEOUSPHOTOCATALYSISANOVERVIEW..pdf.

[6] A. C. Rodrigues, M. Boroski, J. C. Garcia, N. S. Shimada, J. Nozaki and N. Hioka. Treatment of paper pulp and paper mill wastewater by coagulation-flocculation followed by heterogeneous photocatalysis. *J. Photochem. Photobio. A: Chem.* 2008, **194**: 1-10.

[7] M. Perez, F. Torrades, J. Peral, C. Lizama, C. Bravo, S. Casas, J. Freer and H. D. Mansilla. Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent. *Appl. Cata. B: Env.* 2001, **33**: 89-96.

[8] L. K. Boyd and C. B. Almquist. The application of photocatalysis on TiO_2 for degrading COD in paper mill wastewaters. *TAPPI J.* 2004, **3(9)**: 9-15.

[9] P. Kumar, S. Kumar, N. K. Bhardwaj and A. K. Choudhary. Optimization of process parameters for the photocatalytic treatment of paper mill wastewater. *Env. Eng. Manag. J.,* In press, 2011.

[10] L. S. Clesceri, A. E. Greenberg and A. D. Eaton (eds). *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association: Washington, DC, USA, 20th ed., 1998.

[11] N. V. Klassen, D. Marchington and C. E. McGowan. H_2O_2 determination by the I_3^- method and by $KMnO_4$ titration. *Analy. Chem.* 1994, **66**: 2921-2925.

[12] P. R. Gogate and A. B. Pandit. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv. Env. Res.* 2004, **8**: 501–551.

[13] M. Perez, F. Torrades, J. A. Garcia-Hortal, X. Domenech and J. Peral. Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation. *J. Photochem. Photobio. A: Chem.* 1997, **109**: 281-286.

[14] I. A. Balcioglu and I. Arslan. Application of photocatalytic oxidation treatment to pretreated and raw effluents from the kraft bleaching process and textile industry. *Env. Pollu.* 1998, **103**: 261-268.

[15] I. A. Balcioglu and F. Cecen. Treatability of kraft pulp bleaching wastewater by biochemical and photocatalytic oxidation. *Wat. Sci. Tech.* 1999, **40(1)**: 281-288.

[16] A. M. Amat, A. Arques, F. Lopez and M. A. Miranda. Solar photocatalysis to remove paper mill wastewater pollutants. *Sol. Ener.* 2005, **79**: 393-401.

[17] E. Chamarro, A. Marco and S. Esplugas. Use of Fenton reagent to improve the biodegradability of effluents. *Wat. Res.* 2001, **35**: 1995–1999.

[18] M. C. Yeber, J. Rodrguez, J. Baeza, J. Freer, C. Zaror, N. Duran and H. D. Mansilla. Toxicity abatement and biodegradability enhancement of pulp mill bleaching effluent by advanced chemical oxidation. *Wat. Sci. Tech.* 1999, **40**: 337–342.

[19] B. Boman, M. E. B. Frostell and K. Eriksson, Some aspacts of biological treatment of bleached pulp mill effluents. *Nordic Pul. Pap. Res. J.* 1989, **3(1)**: 13-18.

[20] H. Mansilla, M. Yeber, J. Freer, J. Rodriguez and J. Baeza. Homogeneous and heterogeneous advanced oxidation of a bleaching effluent from the pulp and paper industry. *Wat. Sci. Tech.* 1997, **35**: 273–278.

Author Index