

REMOVAL OF ORGANIC CONTAMINANTS IN BLEACHED KRAFT EFFLUENTS USING HETEROGENEOUS PHOTOCATALYSIS AND OZONE

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ABSTRACT

Heterogeneous photocatalysis and ozone treatment have been successfully used to remove low concentrations of organic and halo-organic contaminants in water. This study examines the use of ozone and the photocatalytic treatment for the destruction of organic pollutants in bleached kraft mill effluents (BKME). Reductions in the levels of AOX (adsorbable organic halogen), TOC (total organic carbon), COD (chemical oxygen demand), and color were used as indicators of organic contaminant removal. Two different BKMEs were obtained in a laboratory bench reactor under optimal conditions for the preparation of bleached hardwood pulp from Eucalyptus globulus. One BKME was obtained from the D stage (100% ClO₂) of an elemental-chlorine-free (ECF) AOD bleaching sequence, while the other was obtained from the first D stage (100% ClO₂) in a conventional ECF sequence.

INTRODUCTION

Nearly all of the environmental loading from a modern sulfate pulp mill originates during the first chlorination and the caustic extraction stages of the bleaching process (1). These are responsible for the high levels of TOC (total organic carbon), COD (chemical oxygen demand), color, and chlorinated organics found in bleached kraft mill effluents (BKME). The presence of chlorinated organics in BKME has been recognized as an important environmental issue (2–6). The chlorinated organic compounds are quantified by the surrogate parameter AOX (adsorbable organic halogen). AOX includes compounds that are mutagenic, toxic, and not readily biodegradable. Despite of the controversy about the use of AOX as an effluent quality parameter, the regulatory agencies are setting discharge limits for AOX.

In anticipation of pollution control legislation, kraft mills worldwide are preparing to meet the proposed regulations via two approaches:

1. In-plant process modifications such as extended delignification and substitution of chlorine in the bleaching stage by molecular oxygen, ozone, or hydrogen peroxide
2. Treatment of wastewaters by physical-chemical processes, including chemical oxidation (i.e., ozone).

Both aerobic and anaerobic biological treatment schemes have been applied to individual processes and total plant wastewaters. Indeed, the pulp industry is making a concerted effort to improve the applicability of physical-chemical treatments.

In this paper, we study the application of heterogeneous photocatalysis and ozone to destroy organic contaminants in BKMEs from the first D stage (100% ClO_2) of two ECF (elemental chlorine free) bleach sequences applied to kraft pulp from *Eucalyptus globulus*:

1. An AOD bleach sequence (acid pretreatment (A) followed by an oxygen delignification (O) and chlorine dioxide bleaching (D))
2. A conventional ECF bleach sequence (D(EO)D sequence)

These effluents were chosen because of their increasing prevalence in the production of bleached pulps (7). In addition, the contaminant loads from these ECF bleach sequences are amenable to treatment, which will help pulp mills to comply with increasingly strict environmental regulations (8).

Heterogeneous photocatalysis with TiO_2 has been successfully used in the laboratory to destroy low concentrations of organic and halo-organic contaminants in water. Many works concerning the treatment of organic synthetic samples can be found in the literature (9–15). Other works have demonstrated the effectiveness of the photocatalysis procedure in removing organic BKME contaminants in the laboratory (16–20). Sierka *et al.* (20) reported a combination of photocatalysis and ozone. Other techniques, such as filtration and biological treatment, have also been studied.

The aim of this work, and that of several recently published papers (21–23), is to enhance the biodegradability of BKMEs by means of various combined advanced oxidation processes (AOP). An early work by Tanaka *et al.* (24), dealing with samples of agricultural chemicals, reports the sequential application of photocatalysis and ozonation. More recently, several authors have demonstrated the beneficial effect of a combined ozone and photocatalytic treatment using synthetic samples at low concentrations (25–32).

Heterogeneous photocatalysis involves the irradiation of a semiconductor such as titanium dioxide (TiO_2) with ultraviolet light below 390 nm. Natural (sunlight) or artificial (UV lamps) photon sources can be applied. The radiation stimulates electrons in the valence band of the TiO_2 particles suspended in the wastewater. The excited electrons jump to the conduction band, leaving holes in the valence band. Once formed, the electron (e^-) – hole (h^+) pairs can recombine to generate heat, or they can migrate to the TiO_2 surface and react with dissolved organic or inorganic species in water.

It has been postulated (20, 21, 33–35) that holes react with water and OH^- to produce hydroxyl radicals. The latter can completely oxidize organics (including halogenated organics) to water, carbon dioxide, and mineral acids. Electrons can react with dissolved oxygen to form superoxide anions (O_2^-) that eventually produce hydroxyl radicals ($\text{OH}^\bullet$). Electrons may also react with metals, causing their precipitation on the TiO_2 surface (36–39). The external addition of oxidants such as ozone is expected to enhance the net production of radicals, a fact that would be sustained by increased rates of organic destruction, although the effectiveness of ozone by itself for oxidizing organic compounds is widely documented (23, 37–44). Mansilla *et al.* (21) claim that addition of ozone to heterogeneous systems such as ZnO/UV minimizes the recombination of electron–hole pairs. The electron-withdrawing capacity of ozone can promote the generation of holes.

In this work, photocatalysis alone and in combination with ozonation has been applied to the previously described bleach-plant effluents. Fairly concentrated samples of BKME were treated by sequences of photocatalysis and ozonation or by simultaneous application of both techniques. In the case of the most contaminated effluent (from the first D stage of a (D(EO)D) bleach sequence), hydrolysis in basic media was carried out before the application of photocatalysis. Dorica (45) has reported the removal of organic chlorine from bleach-plant effluents using alkaline hydrolysis. In addition, Milosevich *et al.* (46) demonstrated that neutralization of bleach-plant effluent with lime mud, followed by the addition of an alkaline sulfide process liquor, was a practical, cost-effective method of reducing mill AOX discharge.

EXPERIMENTAL

The experiments were performed with laboratory effluents obtained from two ECF bleaching sequences:

- BKME1: collected from the D stage (100% ClO_2) of an AOD bleaching sequence
- BKME2: obtained from the first D stage (100% ClO_2) in a conventional (D(EO)D) bleaching sequence.

Both BKMEs (bleached kraft mill effluents) were obtained in a laboratory bench reactor under optimal conditions for the preparation of bleached hardwood pulp from *Eucalyptus globulus*.

We also worked with a modified BKME2 that was treated to reduce the load of organic contaminants. The modified effluent was obtained by subjecting the BKME2 to hydrolysis with $\text{Ca}(\text{OH})_2$ (pH 12, during 1 h), which reduced TOC by 70%. This process — carried out at room temperature — has been described elsewhere (42).

The semiconductor used was titanium dioxide (Degussa P. 25). It was predominantly anatase (80% anatase and 20% rutile), as shown by X-ray diffraction. The BET surface area of TiO_2 , determined from nitrogen adsorption (Accusorb 2100 E Micromeritics), was $57.9 \text{ m}^2/\text{g}$. The average particle size, measured by scanning electron microscopy, was 30 nm.

The ozone generator — supplied by Carbueros Metálicos S.A. — was equipped with power control via current settings. A working current of 1 A and a pressure of 0.5 bar were used. To ensure saturation of the system, an ozonized oxygen flow rate of 330 mL/min ($1.5 \text{ g O}_3/\text{h}$) was employed.

Experiments were conducted in a thermostatic Pyrex cell with a capacity of 130 cm³. The reaction mixture inside the cell was maintained in suspension by magnetic stirring. A 125-W Philips HPK mercury vapor lamp was used as a light source. The IR fraction of the beam was removed by the water in the double jacket of the photoreactor. The intensity of the incident light inside the photoreactor, measured with a uranyl actinometer, was 9.2×10^{-5} Einstein/min.

In each experiment, a 100-mL volume of effluent of known pH was placed in the reactor, where the temperature and bubbling gas flow rate had previously been set. Air at an approximate flow rate of 60 mL/min was used. The flow rate was periodically controlled by using a Varian digital flowmeter. The required amount of semiconductor was weighed to the third decimal place on a Bosch S-2000 analytical balance and suspended in the reactor solution. Agitation and light source were switched on, and samples were periodically taken from the reactor by means of an ICO sterile 5-mL syringe and centrifuged on a Centromix S-549 centrifuge. The resulting sample was used to determine TOC. Then AOX, COD, and color were determined after passing the sample through a disposable membrane filter (Schleicher & Schuell) of 0.45- μ m pore size. The membrane filter was tested to ensure that it was not reacting with or holding any of the products we were attempting to measure.

All AOX tests were performed according to SCAN W 9:89 and the method outlined by Torrades *et al.* (47) using a Euroglass ECS 2000 apparatus. The Hach COD test apparatus was used to measure all COD. We validated the Hach results based on results obtained using CPPA Standard Method H.3 (1991).

Total organic carbon (TOC) concentrations were measured on a Shimadzu TOC 5000. All color measurements were conducted in a double-beam spectrophotometer (SP8-300 Pye Unicam) at the wavelength of 465 nm using cuvettes of 10-mm light path, according to CPPS Standard Method H.5 (48).

RESULTS AND DISCUSSION

The BKME1, obtained as described in the experimental section, had the following global parameter values: TOC = 306 mg/L; COD = 515 mg/L; AOX = 27.7 mg/L; and color = 250 c.u. (color units).

Figure 1 shows the changes in TOC after prolonged (20 h) photocatalytic treatment of BKME1 effluent in the presence of TiO₂. As can be seen, an 88% TOC reduction (from 306 to 36.9 mg/L) was obtained. A detailed analysis of the data shows three different zones of TOC removal. In the first minutes, an important decrease in TOC (100 mg/L, approx.) is noticed, largely due to dark adsorption of the organic contaminants onto the TiO₂ surface. Two experiments were carried out to verify that the initial decrease of TOC is a consequence of adsorption and saturation of the catalyst surface. A decrease of 3.2% in TOC was obtained after 15 min of stirring our effluent with TiO₂ in the dark. Longer reaction times did not produce further reduction. The same experiment under light irradiation produced an initial reduction of 5.3% of TOC values, followed by low decrease of TOC for longer reaction times.

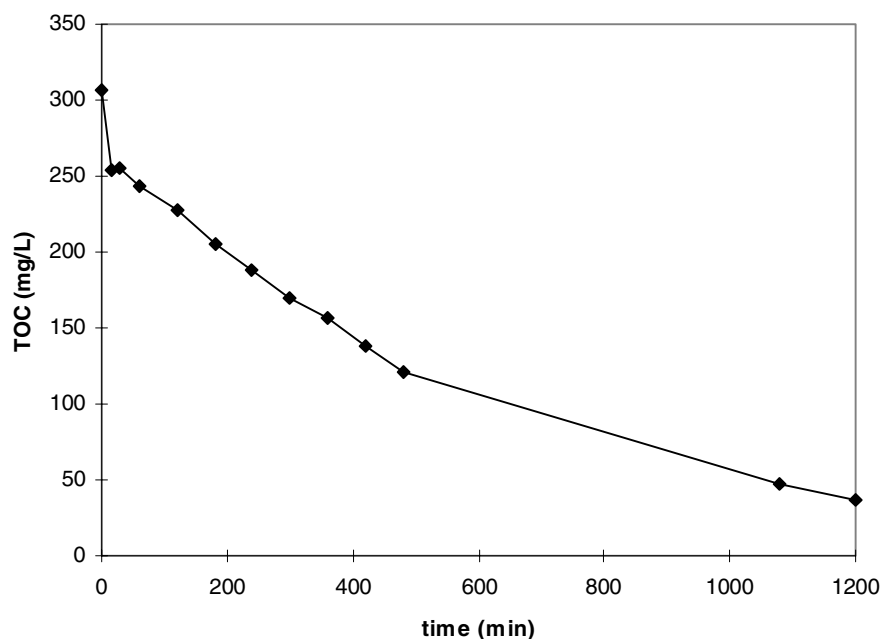


Figure 1. Decrease of total organic carbon (TOC) with run time for photocatalytic treatment of BKME1 effluent (run time = 20 h, $[\text{TiO}_2] = 6 \text{ g/L}$, $\text{pH} = 3$, UV irradiation, air flow rate = 60 mL/min , $T = 25^\circ\text{C}$)

After this initial TOC reduction, zero-order kinetics is observed. The zero-order behavior can be explained by considering the Langmuir–Hinshelwood mechanism of heterogeneous reactions in the presence of a large concentration of reactants (49). For sufficiently long reaction times, the reaction slows down, and removal of the final remnants of TOC becomes difficult. The reductions obtained for the other reaction indicators were 100% in color, 92.5% in AOX, and 85% in COD. Thus, the TOC reduction is associated with a complete removal of colored compounds and a drastic degradation of the toxic halogenated compounds.

The BKME2, obtained as described in the experimental section, had the following global parameter values: TOC = 1380 mg/L ; COD = 3700 mg/L ; AOX = 69.8 mg/L ; and color = 7030 c.u. Note that the BKME2 effluent is clearly more contaminated than BKME1.

The BKME2 effluent was also subjected to a prolonged (52 h) photocatalytic treatment with TiO_2 . **Figure 2** shows changes in TOC during the reaction. A moderate 38% reduction in TOC (from 1380 to 857.3 mg/L) is observed over the 52-h reaction time. As in the case with BKME1, there is a large initial decrease in TOC (more than 200 mg/L) during the first 500 min, indicating the adsorption of dark organic matter onto the catalyst surface. Afterwards, the reaction slows down, and complete TOC removal from BKME2 seems too difficult to accomplish. The large differences in reactivity can be explained by the difference in initial TOC content for the two BKMEs. The high TOC content in BKME2 produces a large concentration of organic intermediates that remain on the TiO_2 surface and inhibit the degradation of the original compounds. The same should happen with the less-loaded BKME1, but almost complete TOC removal is obtained before the system is inhibited. The other reaction indicators — AOX, COD, and color — showed reductions of 50%, 57.5%, and 65%, respectively. These reductions are noticeably larger than the TOC reduction, demonstrating that color and AOX are mainly present in the compounds initially existing in solution.

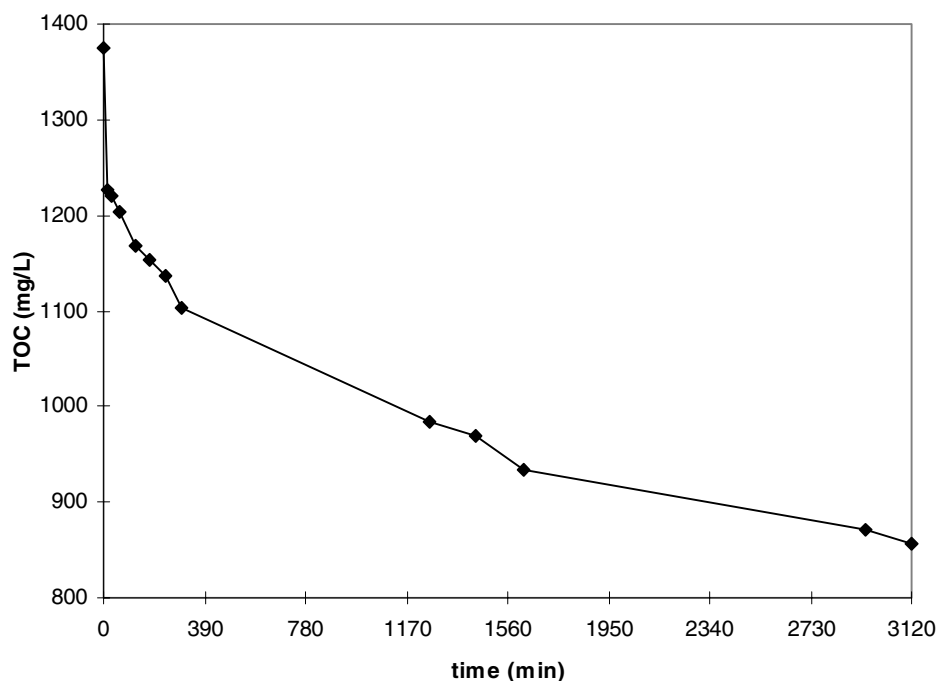


Figure 2. Decrease of total organic carbon (TOC) with run time for photocatalytic treatment of BKME2 effluent (run time = 52 h, $[TiO_2] = 6$ g/L, pH = 3, UV irradiation, air flow rate = 60 mL/min, T = 25°C)

While the extent of TOC degradation in the BKME2 effluent is noticeable, photocatalytic treatment alone would be inadequate to comply with future environmental regulations (8). Consequently, a combination of treatments is needed to ensure adequate degradation of the effluent.

Hydrolysis of BKME2 effluent followed by photocatalysis resulted in a 70% reduction of TOC (from 1380 to 417 mg/L). Alkaline hydrolysis involves a precipitation process that has a significant impact on contaminant removal, with precipitation accounting for about 50% of TOC reduction. The removal of the remaining TOC was assayed by simultaneous use of ozonation and photocatalysis. As pointed out earlier, recent works have shown that this combination can improve removal of TOC through the synergetic effects between the two oxidation techniques (22–29). The beneficial consequences of such a combination can be envisaged from another perspective: O_3 /UV (simultaneous use of O_3 and ultraviolet light) is a well-proven technique of BKME treatment, but the use of 254-nm UV light increases its running cost. The addition of TiO_2 (a cheap and stable catalyst) improves the ozonation yields while using less-energetic UVA photons.

In this way, after filtration of the precipitate and adjustment of the remaining aqueous phase to pH 3, the following sequences of treatment were tested on BKME2 effluent after alkaline hydrolysis:

- Photocatalysis followed by ozonation (Ph- O_3)
- Ozonation followed by photocatalysis (O_3 -Ph)
- Simultaneous ozonation and photocatalysis (O_3 +Ph).

The photocatalytic treatment in sequences Ph-O₃ and O₃-Ph lasted 150 min, and the ozonation treatment was 180 min. The simultaneous treatment (O₃+Ph) lasted 150 min. The results obtained in these experiments are shown in **Figure 3**. As can be seen, reductions of more than 80% of TOC are readily attainable with the three sequences, and the slopes of the curves suggest no difficulties in attaining further TOC reduction at longer reaction times. Data in Figure 3 show a major synergistic effect. The O₃+Ph sequence resulted in the same reduction of the contaminant load obtained in the sequences Ph-O₃ and O₃-Ph, but in a shorter time (150 min for O₃+Ph vs. 330 min for Ph-O₃ and O₃-Ph). This behavior has not been reported previously, and it seems of obvious interest from an applications point of view. It is also remarkable that previous photocatalytic treatment of the polluted samples favors the subsequent ozonation, as can be inferred from the difference of slopes of the ozonation curves in sequences O₃-Ph and Ph-O₃. The reduction of the reaction time implies less ozone demand and a consequent reduction in the cost of the global process.

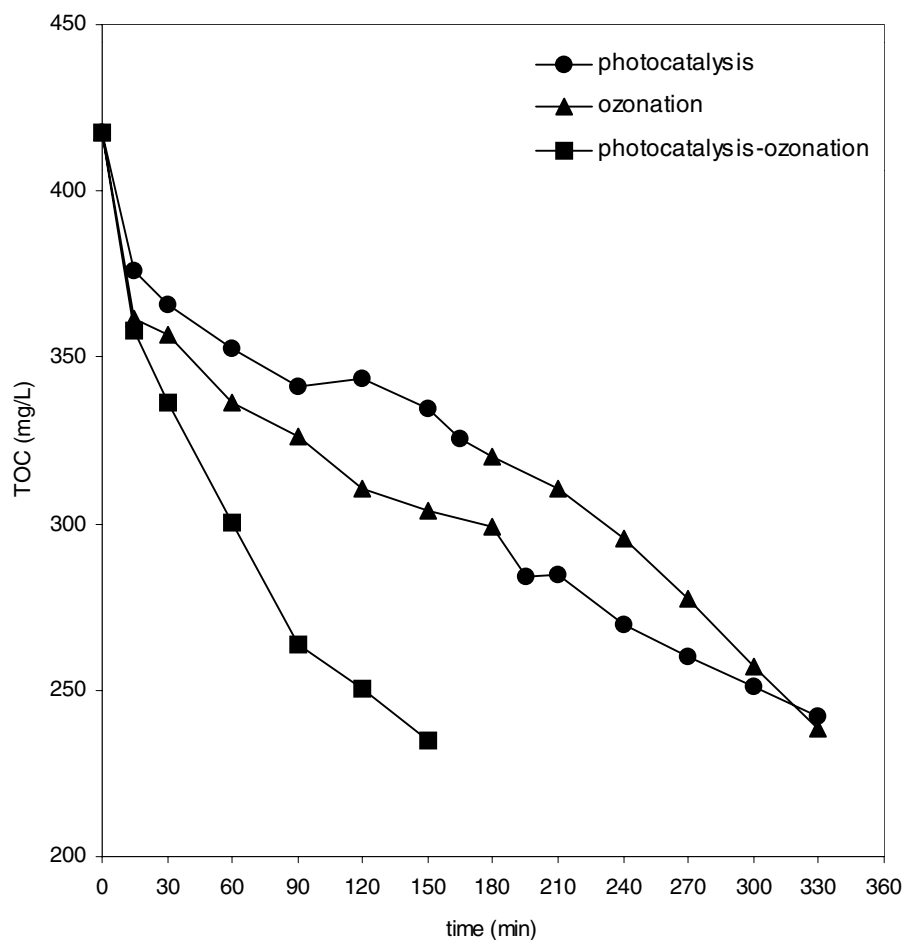


Figure 3. Decrease of total organic carbon (TOC) with run time for combined photocatalytic and ozonation treatments of BKME2 effluent (run time = 6 h, [TiO₂] = 6 g/L, pH = 3, UV irradiation, 1.5 g O₃/h, air flow rate = 330 mL/min, T = 25°C)

The values of AOX and COD after the different treatments are given in **Table I**. In all cases, the reduction exceeded 85%. A fully decolorized effluent was obtained with each of the three sequences (O₃-Ph, Ph-O₃, and O₃+Ph).

	TREATMENTS ^a					
	Hydrolysis	O ₃ (175 min)	O ₃ – Ph (330 min)	Ph (150 min)	Ph – O ₃ (330 min)	Ph + O ₃ (150 min)
AOX, mg/L	23	10.33	8.59	14	7.81	9.87
Reduction ^b , %	...	...	88	...	89	86
COD, mg/L	905	626	485	751	402	440
Reduction ^b , %	...	...	87	...	89	88

^a Ph: photocatalytic treatment; O₃: ozone treatment
^b Including previous hydrolysis

Table I. Reduction of AOX and COD for various treatments of BKME2 effluent.

CONCLUSIONS

Heterogeneous photocatalysis and ozone are known to be effective techniques for destroying low levels of organic pollutants in aqueous systems. This paper examines the capability of these techniques to destroy organic contaminants in bleached kraft mill effluents (BKME). A 20-h photocatalytic treatment removed all of the color and most of the TOC, AOX, and COD in a lightly loaded effluent obtained from the D stage (100% ClO₂) of an AOD bleach sequence. For an effluent with a higher contaminant load — like the one (BKME2) obtained from the chlorine dioxide (bleaching) stage (D) in a conventional ECF sequence — the best treatment is the one that takes advantage of a previous hydrolysis and the synergistic effect of simultaneous photocatalysis and ozonation. Similar levels of TOC removal were obtained in the sequences hydrolysis–Ph–O₃ and hydrolysis–O₃–Ph, although for larger reaction times. The TOC, COD, and AOX reductions in the treated effluents were above 80% in all cases, and the effluents were always fully decolorized.

LITERATURE CITED

1. Välttilä, O., “Discharges from a modern kraft pulping process and their treatability with aerobic biological methods,” *Proceedings of International Conference on Bleached Kraft Mills*, Feb. 4–7, Melbourne, Australia, 1991.
2. Bonsor, N., McCubbin, N., and Sprague, J. B., “Kraft mill effluents in Ontario,” Report to Technical Advisory Committee, Pulp and Paper Section of MISA, Ontario Ministry of Environment, Toronto, 1988.
3. Reeve, D. W. and Earl, P. F., *Pulp Paper Can.* 90(4): T128(1989).
4. Stromdahl, I. and Lovblad, R., *Svensk Papperstid.* 90(6): 52(1987).
5. Norrstrom, H., “Reducing the discharges to water — technical objectives,” *Proceedings 2nd IAWPRC Symposium on Forest Industry Wastewaters*, Pergamon Press, Oxford, UK, 1987.
6. Huber, L. and Baumung, H., “Requirements for the treatments of effluents from pulp mills in the FRG,” *Proceedings 2nd IAWPRC Symposium on Forest Industry Wastewaters*, Pergamon Press, Oxford, UK, 1987.
7. Pryke, D. C. and McKenzie, D. J., *Pulp Paper Can.* 97(1): 27(1996).
8. Lescot, J. C. and Jappinen, H., *Appita* 47(4): 330(1994).

9. Hoffmann, M. R., Martin, S. T., Choi, W., and Bahnemann, D. W., "Environmental applications of semiconductor photocatalysis," *Chem. Rev.* 95: 69(1995).
10. Ollis, D. F., "Solar-assisted photocatalysis for water purification: Issues, data, questions," in *Photochemical Conversion and Storage of Solar Energy* (E. Pelizzetti and M. Schiavello, Eds.), Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991.
11. Serpone, N., Pelizzetti, E., and Hidaka, H., "Heterogeneous photocatalysis: Issues, questions, answers and successes," *Proceedings of 9th International Conference on Solar Energy, IPS-9* (Z. W. Tian and Y. Cao, Eds.), International Academic Publishers, Beijing, China, 1992, pp. 33–73.
12. Ollis, D. F., Pelizzetti, E., and Serpone, N., *Envir. Sci. Technol.* 25: 1523(1991).
13. Fox, M. A. and Dulay, M. T., *Chem. Rev.* 93: 341(1993).
14. Matthews, R. W., *Solar Energy* 38: 405(1982).
15. *Homogeneous and Heterogeneous Photocatalysis* (E. Pelizzetti and N. Serpone, Eds.), Dordrecht Reidel, Amsterdam, 1986.
16. Ollis, D. F., *Envir. Sci. Technol.* 19(6): 480(1985).
17. Okamoto, K., Yamamoto, H., Tanaka, M., and Itaya, A., *Bull. Chem. Soc. Japan* 58: 2015(1985).
18. Matthews, R. W., *Water Res.* 20(5): 569(1986).
19. Turchi, C. S., Edmundson, L., and Ollis, D. F., *Proceedings of 5th International Symposium on Wood and Pulp Chemistry*, TAPPI PRESS, Atlanta, 1989.
20. Sierka, R. A. and Bryant, C. W., *Photocatalytic Purification and Treatment of Water and Air* (D. F. Ollis and H. Al-Ekabi, Eds.), Elsevier Science, New York, 1993, p. 275.
21. Mansilla, H. D., Yeber, M. C., Freer, J., Rodríguez, J., and Baeza, J., *Water Sci. Technol.* 35(4): 273(1997).
22. Yeber, M. C., Rodríguez, J., Freer, J., Baeza, J., Durán, N., and Mansilla, H. D., *Chemosphere* 39(10): 1679(1999).
23. Yeber, M. C., Rodríguez, J., Baeza, J., Freer, J., Zaror, C., Durán, N., and Mansilla, H. D., *Water Sci. Technol.* 40(11): 337(1999).
24. Tanaka, K., Abe, K., Sheng, C. Y., and Misanaga, T., *Envir. Sci. Technol.* 26(12): 2534(1992).
25. Sánchez, L., Peral, J., and Domènech, X., *Appl. Catal., B* 19(1): 59(1998).
26. Tanaka, K., Abe, K., and Misanaga, T., *J. Photochem. Photobio. A* 101: 85(1996).
27. Muller, T. S., Sun, Z., Kumar, G., Itoh, K., and Murabayashi, M., *Chemosphere* 36: 2043(1998).
28. Klare, M., Waldner, G., Bauer, R., Jacobs, H., and Broekaert, J. A. C., *Chemosphere* 38: 2013(1999).
29. Hay, S. and Obee, T. N., *J. Adv. Oxidation Technol.* 4: 209(1999).
30. Krapfenbauer, K. and Getoff, N., *Radiat. Phys. Chem.* 55: 385(1999).
31. Rivas, L., Bellobono, I. R., and Ascari, F., *Chemosphere* 37: 1033(1998).
32. Gratson, D. A., Nimlos, M. R., and Wolfrum, E. J., "Photocatalytic oxidation of gas-phase BTEX-contaminated waste streams," *Air Waste Management Association Annual Meeting Proceedings*, 4B(88): 11(1995).
33. Prairie, M. R., Evans, L. R., and Martinez, S. L., "Destruction of organics and removal of heavy metals in water via TiO₂ photocatalysis," *Chemical Oxidation: Technology for the Nineties, Second International Symposium*, Technomic, Lancaster, PA, 1994, pp. 428–441.
34. Fox, M. A., *Acc. Chem. Res.* 16: 314(1983).
35. Matthews, R. W., *J. Catalysis* 111: 264(1988).
36. Clark, W. C. and Vonjigidis, A. G., *J. Catalysis* 4: 691(1965).
37. Mollers, F., Tolle, H. J., and Memming, R., *J. Electrochem. Soc.* 121: 1160(1974).

38. Netzer, A. and Bowers, A., *1st International Symposium on Ozone for Water and Wastewater Treatment*, International Ozone Assn., Vienna, 1975.
39. Prengle, H. W., *Hydrocarbon Proc.* 10: 82(1975).
40. McGuire, M. L., *Ozone Technology Symposium Proceedings*, International Ozone Institute, Los Angeles, 1978.
41. Macur, G. J., *35th Industrial Waste Conference Proceedings*, West Lafayette, 1981.
42. Coburn, L. A., Englande, A. J., Lockwood, M. P., and Collins, T., "Kraft bleach plant effluent by ultraviolet/oxidation process," *TAPPI 1984 Environmental Conference Proceedings*, TAPPI PRESS, Atlanta, p. 277.
43. Herberl, R., Urban, W., Gehringer, W., and Szinovatz, W., "Research on biological and advanced treatment of pulp-bleaching effluents," *Proceedings 3rd IAWPRC Symposium on Forest Industry Wastewaters*, Pergamon Press, Oxford, UK, 1991.
44. Saunamaki, R. and Sorvari, J., *Nordic Pulp Paper Res. J.* 7(3): 113(1992).
45. Dorica, J., *J. Pulp Paper Sci.* 18(6): 231(1992).
46. Milosevich, G. M. and Hill, D. A., *Pulp Paper Can.* 93(3): 61(1992).
47. Torrades, F., Riva, M. C., Torres, S., Garcia Hortal, J. A., Domènech, X., Peral, J., and Pérez, M., *Anal. Chim. Acta* 333: 139(1996).
48. CPPA Standard Method H.5, "Color of pulp mill effluents" (revised Aug. 1993), Canadian Pulp and Paper Association, Montreal.
49. Ollis, D. F., Pelizzetti, E., and Serpone, N., in *Photocatalysis Fundamentals and Applications* (N. Serpone and E. Pelizzetti, Eds.), Wiley, New York, 1989, p. 603.

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