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***DEGRADATION OF ORGANIC COMPOUNDS IN PAPER AND
TEXTILE INDUSTRIAL WASTEWATERS BY ADVANCED
OXIDATION PROCESSES***

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Treatment of bleached Kraft mill effluents and polychlorinated phenolic compounds with ozonation

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Abstract

The effect that the simultaneous use of ozone, UVA or visible light, and small quantities of Fe(II)/ Fe(III) ions in solution has on the degradation rate of the organic content of a bleaching Kraft mill effluent is studied. The same treatment is applied to synthetic samples of polychlorinated phenolic compounds, because these are one of the main compound families found in real bleaching Kraft mill effluents. In order to improve the treatment efficiency and lowering the cost of the process several other strategies are investigated. It was found that a previous irradiation of the wastewater or the synthetic sample in absence of ozone clearly improves the rate of removal of organic pollutants during the subsequent ozonation step.

Keywords: Cellulose bleaching effluent, chlorinated phenols, Ozonation, UVA, Iron.

Introduction

Ozonation, often combined with H₂O₂, UVA, or both, and even with heterogeneous photocatalytic processes, has been widely applied to wastewater treatment.¹⁻⁹ The mechanism of the oxidation of organic compounds by ozone and in the dark has been carefully studied by Hoigne et al.¹⁰⁻¹²

Ozone can react with the organic load present in the wastewaters by two different ways: (a) direct reaction (reaction (1)), a process that is highly selective toward aromatic compounds and rather slow; (b) indirect reaction through OH radicals (reactions (2) and (3)), that comes from the fragmentation of the HO₃[•] specie:



It should be noted that the ozonide ion (O₃^{•-}) which is necessary for the indirect pathway, is also a reaction product of ozone and OH⁻. Consequently, a basic media promotes the O₃^{•-} generation as the presence of organic matter do in reaction (1).

The OH radicals formation yield predicted by this model, as calculated by Hoigné et.al., is 0.65 molecules of OH for every molecule of ozone decomposed.

Since the oxidative power (2.8 V vs. NHE) of the OH radical is higher than the oxidative power (2.08 V vs. NHE) of ozone it is expected that most of the organic degradation is achieved through the indirect reaction.

One disadvantage of the ozonation process that must be considered is the high electrical energy demand for the generation of the chemical reagent.¹³ Therefore, the total costs of ozonation are usually high.

The beneficial effect of carrying out ozonation under irradiation has been explored by Peyton et al.¹⁴ O₃/UV is a complex oxidation process because OH radicals can be produced through different reaction pathways. Recently, studies found that sunlight produces a noticeable increase of the rate of reactions activated by ozone, along with a complementary improvement on the rates of organic removal and a cost decrease of the treatment. The simultaneous use of sunlight and Fe (II) ions in solution, known to catalytically decompose ozone, has also been explored.¹⁵

In the present paper ozonation will be applied to the treatment of bleaching paper pulp effluents produced in the Kraft mill industry in order to reduce the amount of organic contaminants present in the industrial wastewater at a minimum cost. Bleaching effluent disposal has a high contaminant potential,¹⁶ due to their content in chlorinated phenols and polyphenolic compounds, among other toxic organics. These compounds are difficult to eliminate by conventional wastewater treatment processes and are source of environmental concern due to the risk they pose to the aquatic environment.¹⁶⁻¹⁸ An effluent coming from stage C₈₀D₂₀ (20% of ClO₂ substitution) of a conventional bleaching sequence applied to kraft pulp from 90% of *Eucalyptus globulus* and 10 % of *Eucalyptus grandis* was chosen. Spectrophotometric analyses detected 2,4-dichlorophenol among the polychlorinated phenolic compounds present in the studied effluent. Since this result is in concordance with previous studies of the typical composition of bleaching kraft pulp effluents,^{16,19} a 2,4-dichlorophenol synthetic sample was also investigated.

2,4-Dichlorophenol is one of the 129 priority pollutants listed by the U.S. EPA.^{20, 21} Due to the fact that this pollutant has adverse effects on aquatic life, its removal have been actively investigated. 2,4-DCP can be degraded by either biological methods or physicochemical processes.²² Several days to months are usually required for complete removal of 2,4-DCP by biological methods.

Experimental

The effluents used in the present research were obtained from the chlorination step of the bleaching sequence (D₂₀C₈₀)(EO)D₁D₂ applied to Kraft paper pulp of *Eucalyptus globulus* (90%) and *Eucalyptus grandis* (10%), which was supplied by a Spanish paper manufacturer. In order to reduce the level of organic contaminants, hydrolysis of the wastewaters with Ca(OH)₂ (pH=12, 1 hour) was carried out. After hydrolysis the effluent was stored at - 4°C.

The rest of the chemicals used were, at least, of reagent grade. Analytical grade heptahydrated ferrous sulfate was purchased from Aldrich and was used as received. Analytical grade 2,4-dichlorophenol was purchased from Aldrich and was used as a synthetic sample of 100 g·L⁻¹. Solutions were prepared with deionized water obtained from a Millipore Mili-Q system.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm³ capacity. The reaction mixture inside the cell, consisting of 100 ml of organic effluent and the precise amount of reagents, was continuously stirred with a magnetic bar. In the main experiments the temperature was maintained at 25.0±0.1°C. A 6 W Philips black-

light fluorescent lamp was used as light source. The intensity of the incident light inside the photoreactor, measured employing a uranyl actinometer, was $1.383 \cdot 10^{-9}$ Einstein \cdot s $^{-1}$.

Ozone was produced by a Sander Labor-Ozonisator 301.7, fed with a pure oxygen stream. The resulting ozone and oxygen mixture was immediately bubbled through the bleaching effluent by means of a metallic diffuser. The generator is equipped with power control via current settings. A working current of 1 A and a pressure of 0.5 bar were used. An ozonized oxygen flow-rate of 330 mL \cdot min $^{-1}$ (1.5 g O₃ \cdot h $^{-1}$) was employed to ensure saturation of the system. The amount of ozone generated was determined by iodometry.

Total organic carbon (TOC) of initial and irradiated samples was determined with a Shimadzu 5000 TOC analyzer. Color determination was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells and referenced to a Pt-Co standard solution, according to standard H.5 of the Canadian Pulp and Paper Association (CPPA). Chemical Oxygen Demand (COD) was determined by standardized methodology (EPA 00340).

For the analysis of low molecular weight compounds dissolved in the effluent, a HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector was used. The GC-MS analysis was carried out with ionization of electronic impact, 70 eV, and the spectra were recorded in the interval 40 – 600 amu. One liter of the sample was filtered with Speedisk[®] membrane (J.T. Baker) following the EPA 525 procedure. Samples were reconstituted to 100 μ L in dichloromethane and 1 μ L was injected in the GC. Identifications were carried out with the aid of the data base library WILEY (275,000 spectra) and NIST (130,000 spectra) and with a customized database generated in the UAB laboratory. A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with the following dimensions 30 m, 250 μ m, 0.25 μ m was used. The temperature program used during the GC-MS analysis ramped as follows: 70 $^{\circ}$ C (3 min), 5 $^{\circ}$ C \cdot min $^{-1}$ until 270 $^{\circ}$ C (30 min). The sample injection was carried out with a 0.6 min of splitless time at 250 $^{\circ}$ C. The carrier was helium with a flow rate of 1.3 mL \cdot min $^{-1}$.

Results and discussion

After alkaline hydrolysis the bleaching effluent has the global parameters summarized in Table 1, i.e., the effluent has a high COD and TOC. Spectrophotometric analysis of the effluent allows determination of the structure of some low molecular weight compounds. The mass spectra and the identified structures are shown in Table 2 and Figure 1, respectively. All the substances found show a high degree of chlorination. This agrees with structures found and reported by other authors.^{16,19,23} Among the

polychlorinated phenolic compounds detected 2,4-dichlorophenol has been chosen to be studied as a synthetic sample.

Table 1. *Initial characterization parameters of the bleaching Kraft mill effluent after hydrolysis pretreatment.*

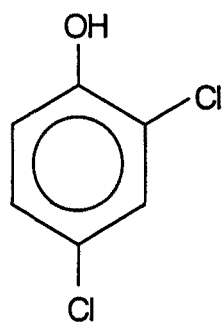
Parameter	Value
TOC (ppm)	441±8*
COD (mg·L ⁻¹ O ₂)	1384±24*
Color (mg·L ⁻¹ Pt)	197±25*

*(n = 4, α = 0.05)

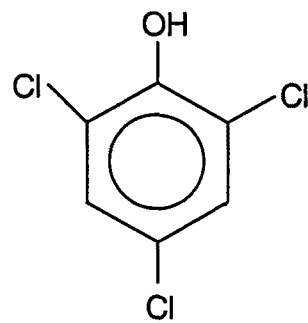
Table 2. *Low molecular weight compounds identified in the bleaching Kraft mill effluent after hydrolysis pretreatment.*

# ^a	rt ^b	mol wt	main fragments	m/z (relative abundance)
1	10.09	162	166 (10), 164 (61), 163 (8), 162 (100), 126 (8), 100 (14), 99 (16), 98 (32), 63 (33), 62 (13), 61 (7)	
2	15.03	196	200 (15), 198 (49), 196 (51), 162 (7), 160 (7), 158 (5), 132 (12), 99 (15), 97 (31)	
3	18.25	192	196 (14), 194 (50), 192 (78), 181 (15), 179 (75), 177 (100), 151 (42), 149 (75), 113 (46)	
4	20.60	226	230 (16), 228 (48), 226 (52), 215 (31), 213 (96), 211 (100), 187 (13), 185 (45), 183 (51), 149 (34), 147 (54), 121 (13), 119 (20)	
5	24.88	260	266 (8), 264 (34), 262 (70), 260 (55), 251 (11), 249 (49), 247 (100), 245 (81), 223 (18), 221 (24), 219 (48), 217 (33), 185 (7), 183 (28), 181 (30)	
6	25.16	256	260 (29), 258 (95), 256 (100), 245 (19), 243 (63), 241 (67), 215 (27), 213 (30), 202 (19), 200 (60), 198 (65), 197 (28), 195 (28)	

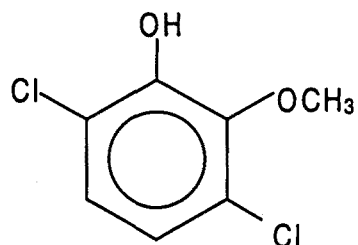
^acompound number. ^bretention time, min.



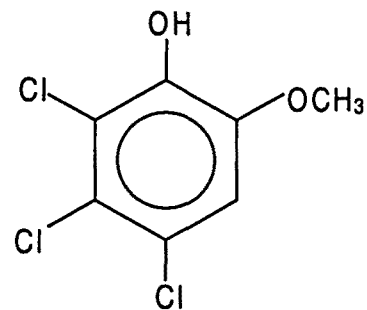
1: 2,4-dichlorophenol



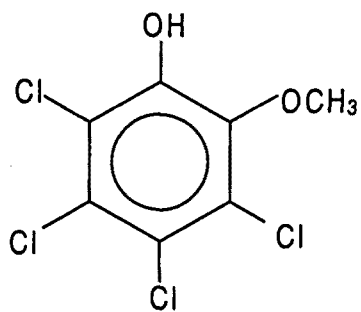
2: 2,4,6-trichlorophenol



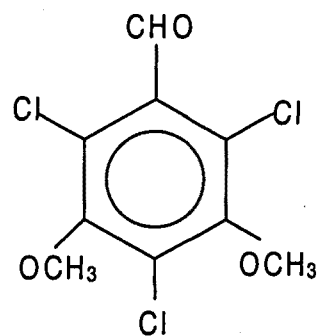
3: 3,6-dichloroguaiacol



4: 4,5,6-trichloroguaiacol



5: tetrachloroguaiacol



6: trichlorosyringol

Figure 1. Structures of some low molecular weight compounds identified by CG-MS analysis in the conventional bleaching effluent after hydrolysis treatment.

Although ozone treatment is able to reach high and fast TOC removal the cost per TOC removal is around ten times higher than other AOPs as Photocatalysis or Fenton and Photo-Fenton reactions.²⁴ Since the main goal of this study is focused on the reduction of ozone demand while achieving the same TOC degradation levels in the treated samples, it will be necessary to estimate the relative cost of the different proposed processes.

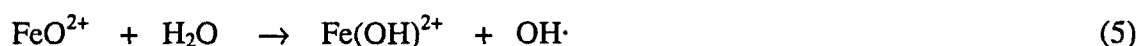
To analyze the cost of the ozonation treatment applied to the bleaching effluent and the synthetic sample the following assumptions were made:

1. In order to account for the different degrees of mineralization the estimative cost of every process was assessed by the costs of kg of TOC removed after 5 hours treatment.
2. Only chemical and energy costs (retail dealer prices) were considered in the estimation. The investment costs for apparatus and buildings are supposed in the same order of magnitude for all the studied treatments and, thus, they were neglected. Energy costs deriving from pumps and process control were also not considered.
3. The costs of additional operations like neutralization, filtration, required in some treatments were not included in the costs assessment.
4. Costs were obtained with non-optimized reactors. Fast reaction rates involve shorter residence times or smaller reactor volumes, as residence time is inversely proportional to the reactor volume.

Energy consumption at the laboratory scale is higher than at an optimized large-scale plant. However, the relative ratio assessment at laboratory scale give us an idea of the reality due to similar savings will be obtained in all the treatments if a large-scale plant will be settled.

Ozonation could be run under solar irradiation¹⁵ this fact turns, generally, energy cost from irradiation into zero. Although solar energy was not used in this study and the results presented have taken into account irradiation cost, it is interesting to notice that treatment costs could be easily decreased by changing to sunlight.

Transition metal ions, as Fe(II), are able to catalyze the decomposition of ozone into hydroxyl radicals²⁵ following the following mechanism proposed in the literature:



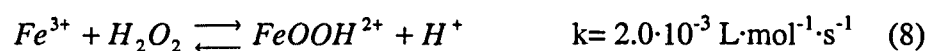
Fe(II) could also support the effect of ozonation by reaction with $\text{HO}_2\cdot$, one of the products of ozone decomposition, generating hydrogen peroxide when pH is below 4.8:



The presence of hydrogen peroxide and Fe (II) leads into the Fenton reaction. The traditionally accepted reaction equation is:



Fe(III) can lead to additional radical production and Fe(II) regeneration in the so-called Fenton like reaction:²⁶



The rate of degradation of the organic pollutants could increase when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photoreduction of Fe(III) to Fe(II) ions by means of the photo-Fenton reaction²⁶⁻²⁸



Moreover, it has been recently demonstrated that the irradiation can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe(III) and organic compounds. This process has been well proven for the complexes formed between Fe(III) and the carboxylic acid moiety.²⁹

Thus, ozone mixture with iron ions and irradiation leads to a combined treatment between ozone and Fenton, Fenton-like and Photo-Fenton reaction.

Figure 2 shows the interesting role that iron plays in presence of ozone and irradiation. In the experiment where 20 ppm of this transition metal is combined with the ozone/UVA mixture, the slope of TOC removal specially increases at the beginning of the treatment, when more contaminant load is present. 90% TOC and 80% COD decrease and more than 90% color reduction, even with the iron lasting in the solution, were the yields of the experiment. As time process reduction is clearly depend on the cost decrease, it should be noted, that the same TOC removal reached after five hours

ozone/UVA treatment, is achieved in presence of iron in just three hours 15 minutes treatment.

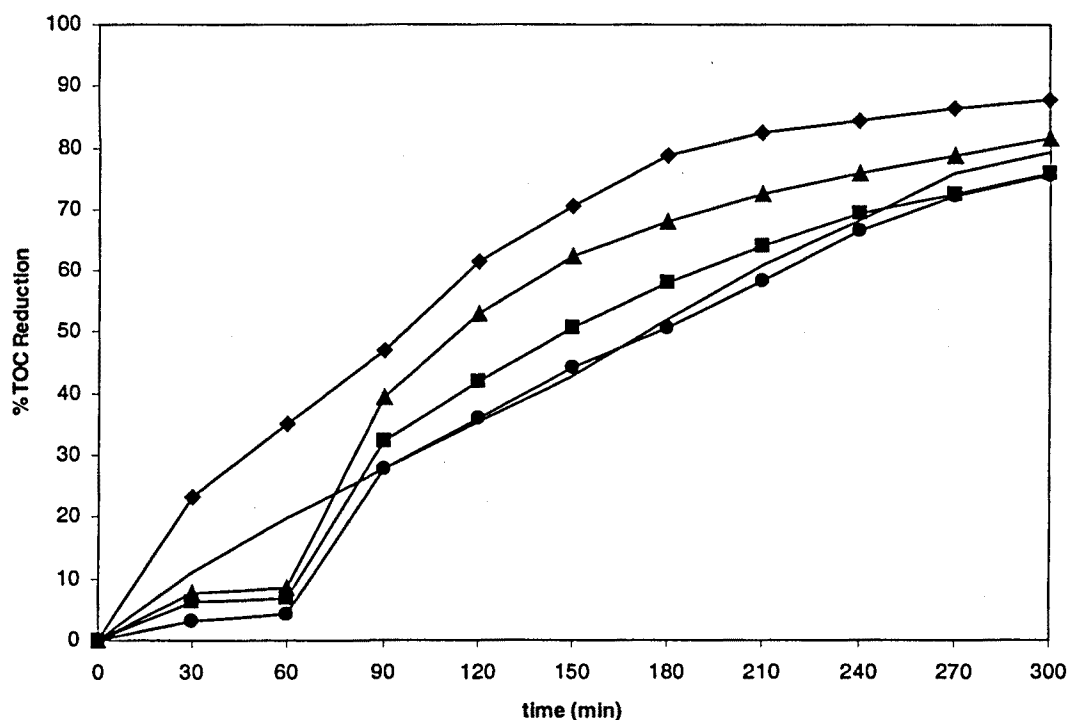


Figure 2. *Percentage of TOC reduction vs. time in a 5 hours treatment and under several experimental conditions: ozonation under UVA irradiation (—); ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II) (◆); one hour stirred 20 mg·L⁻¹ of Fe (II) without irradiation followed by 4 hours ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II) (●); same sequence treatment with 100 mg·L⁻¹ Fe (II) (■); same sequence treatment with 200 mg·L⁻¹ Fe (II) (▲). pH=3, T=25 °C.*

The goal of the other three experiments was to reduce ozone demand with similar TOC removal. Thus, a previous pretreatment was carried out solutions containing different iron concentrations were stirred under dark condition. After one hour of pretreatment, ozone and irradiation were supplied during four more hours more. The levels of TOC removal are similar to the one reached with the ozone/UVA experiment and slightly lower than in the ozone/UVA/Fe(II) treatment. The increase of iron concentration added during the pretreatment step leads to a higher slope during the subsequent ozonation step.

A comparison of the estimated cost per kg of TOC removed in the different experiments was assessed. Figure 3 shows that the ozone/UVA/Fe(II) process is always more

efficient than ozone/UVA. Higher TOC removal is reached with lower cost demand. Among the other treatments few differences were observed: the improving of TOC removal obtained when the iron load is higher just compensate the cost process increase. Consequently, as the increase of Fe(II) load only slightly improve the process, low Fe(II) load will be used in order to decrease the global process cost and to avoid any additional treatment step for iron removal.

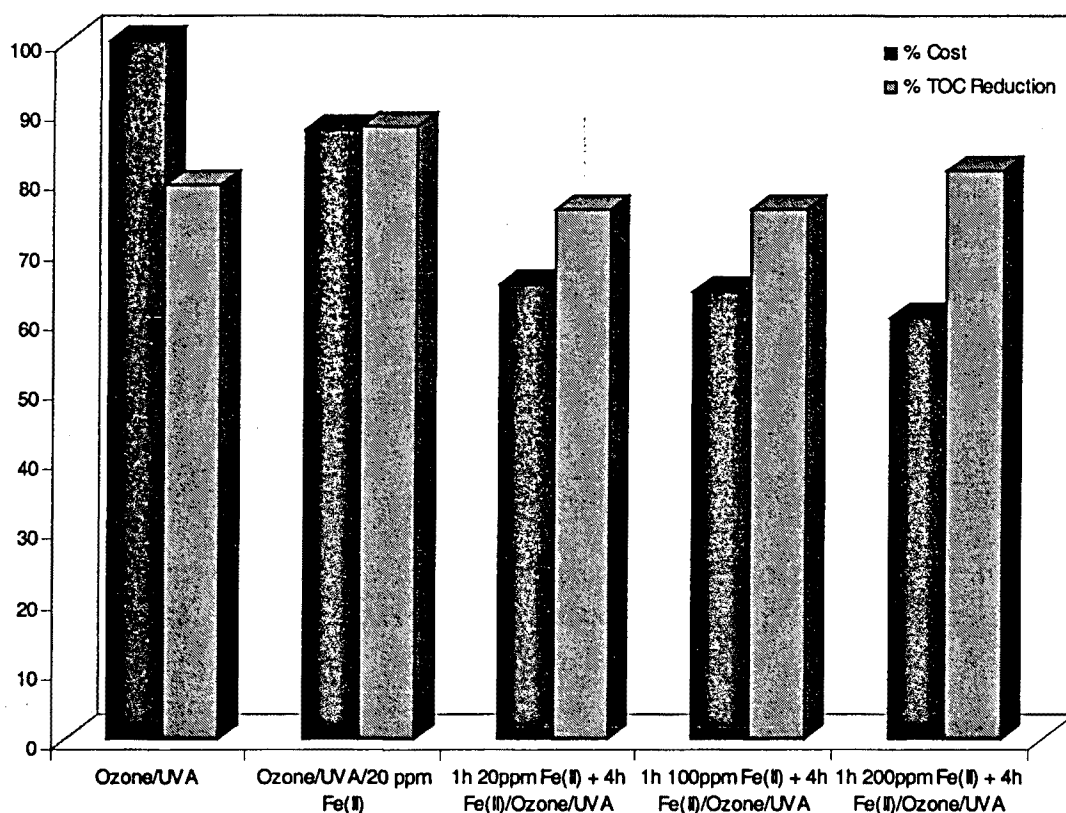


Figure 3. Comparison of the percentage of TOC reduction and estimated costs per kg of TOC removal for the ozonation treatments of Figure 2.

In any case, it has to be said that the sequential treatments (pretreatment in the dark with iron followed with ozone/UVA/Fe(II)) leads to an estimated 35% cost reduction with the same level of TOC removal than the ozone/UVA treatment.

After such interesting result other experiments were carried out in order to achieve even higher cost reductions. In this way a longer time pretreatment in presence of UVA light was carried out. As can be seen in figure 4 pretreatments in the presence of iron and under light irradiation bring larger slopes of TOC removal during the subsequent ozonation step if compared with pretreatments carried out without irradiation. At the

end of the experiments (with and without previous irradiation) similar levels of TOC removal are obtained.

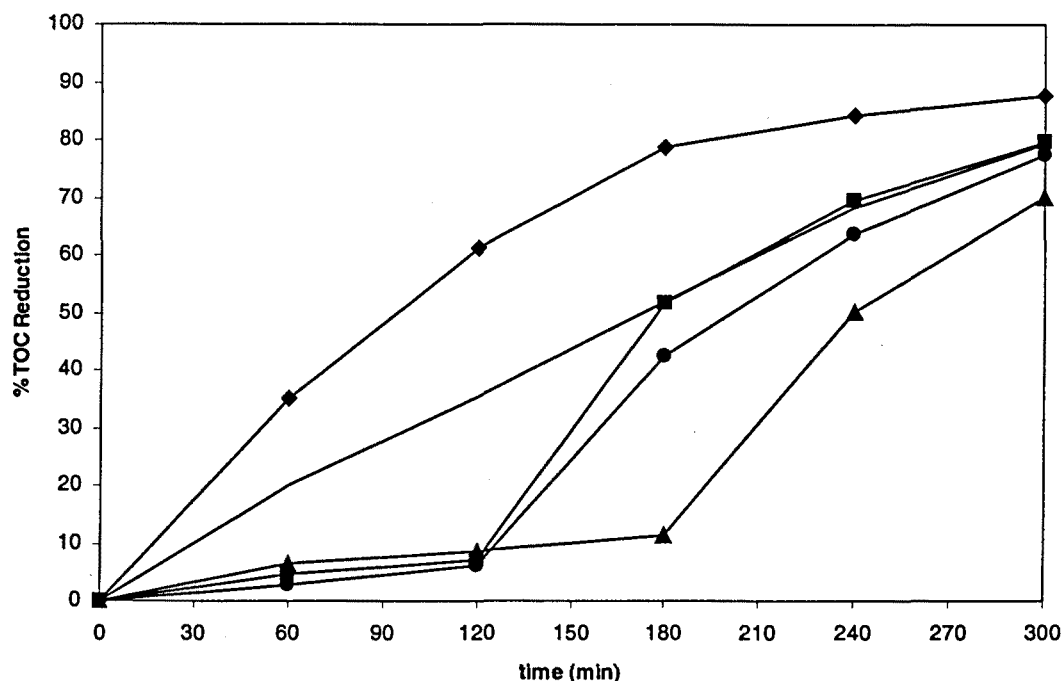


Figure 4. Percentage of TOC reduction vs. under several experimental condition: ozonation under UVA irradiation (—); ozonation under UVA irradiation in presence of $20 \text{ mg}\cdot\text{L}^{-1}$ of Fe (II) (◆); $20 \text{ mg}\cdot\text{L}^{-1}$ Fe(II) solutions stirred during two hour without irradiation followed by three hours ozonation under UVA (●); $20 \text{ mg}\cdot\text{L}^{-1}$ Fe(II) solutions stirred during two hour under irradiation followed by three hours ozonation under (■); $20 \text{ mg}\cdot\text{L}^{-1}$ Fe(II) solution stirred during three hour under irradiation followed by two hours ozonation under UVA (▲). pH=3, T=25 °C.

Pretreatments longer than one hour time give better results, but even longer pretreatment times could bring detrimental effects. As can be seen in figure 4 two hours pretreatment seems to yield higher TOC removal, but a comparison of the estimated cost of treatment should be performed before further conclusions are taken. This is done in figure 5. The sequential experiment with two hours dark pretreatment followed by three hours treatment with the ozone/UVA/Fe(II) mixture produced around a 40% cost reduction for the same order of TOC removal than ozone/UVA treatment.

The same sequential experiment with irradiation pretreatment reached even higher cost reduction, around 50 % for the same order of TOC removal. Consequently, the presence

of UVA irradiation in the pretreatment step lead to interesting results. A reduction of 50% in the cost process is high enough to be taken into account.

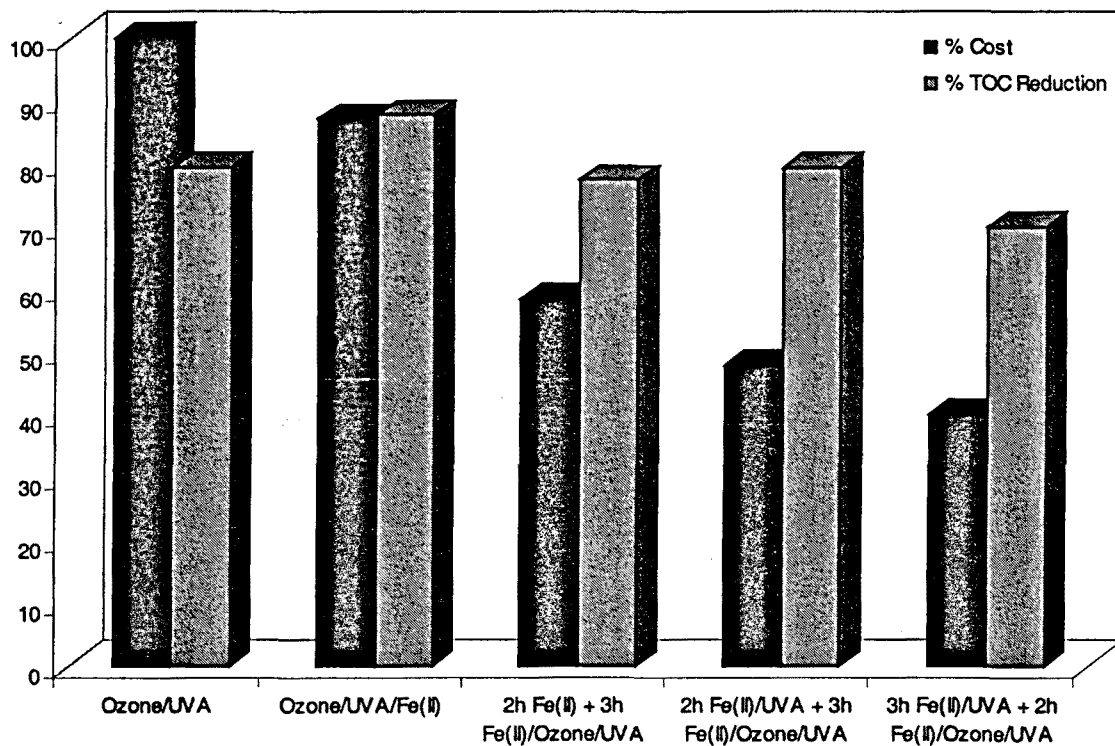


Figure 5. Comparison of the percentage of TOC reduction and estimated costs per kg of TOC removed after various ozonation treatments in presence of 20 g.L⁻¹ of iron 5 hours treatment.

The three hours pretreatment under UVA irradiation and in presence of iron, produced 60% estimated cost reduction, the highest among the experiments compared, but it should be said that TOC removal is around 10 % lower than in the other sequential experiments included in figure 5. The choice of two or three hours pretreatment will be a specific decision for every particular case.

COD decrease in all the treatments summarized in figure 4 is at least around 80 %, reaching 90 % removal in the following experiments: ozonation under UVA irradiation; ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II); two hour stirring of 20 mg·L⁻¹ Fe (II) solutions under irradiation followed for three hours ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II).

The interesting conclusions obtained in the last experiments and the fact that ozone reacts very efficiently with aromatics compounds³⁰ leads to application of such

treatments to a model polychlorinated phenolic compounds: 2,4-dichlorophenol. The choice of this compound was based on its detection in the spectrophotometric analyses of the bleaching effluents and the fact that it is normally cited in the literature^{16,19} as typical component of such wastewaters.

Table 3 summarizes the global analytical parameters of the 2,4-dichlorophenol synthetic sample prepared in the laboratory. Since the increase of iron load during the treatments has no particular effect upon the amount of TOC removal, while the presence of light during the pretreatments brings better result than without irradiation, the experiments carried out with the synthetic sample were carried out with a constant iron load of 20 ppm and the sequential treatments were performed with light driven pretreatments.

Table 3. *Initial characterization parameters of the 2,4-dichlorophenol.*

Parameter	Value
TOC (ppm)	106±1*
COD (mg·L ⁻¹ O ₂)	250±4*
Color (mg·L ⁻¹ Pt)	12±1*

*(n = 4, α = 0.05)

Particular attention was paid to the time of pretreatment and the effect of the presence of iron. Figure 6 summarize the evolution of TOC during the 90 minutes treatment applied to the synthetic solutions.

In concordance with the behavior observed with the industrial bleaching Kraft effluents the presence of iron in the ozone/UVA treatment of the synthetic sample brings an interesting improvement of the process. In presence of iron the COD goes all the way to zero after the 90 minutes treatment while TOC removal is higher than 90%. Sequential treatments bring again outstanding results. In both cases TOC removal is higher than in ozone/UVA treatment. Again longer times pretreatment, that bring a decrease of ozone demand, slightly reduce TOC removal. Removals of COD are higher than 95 % in all the cases.

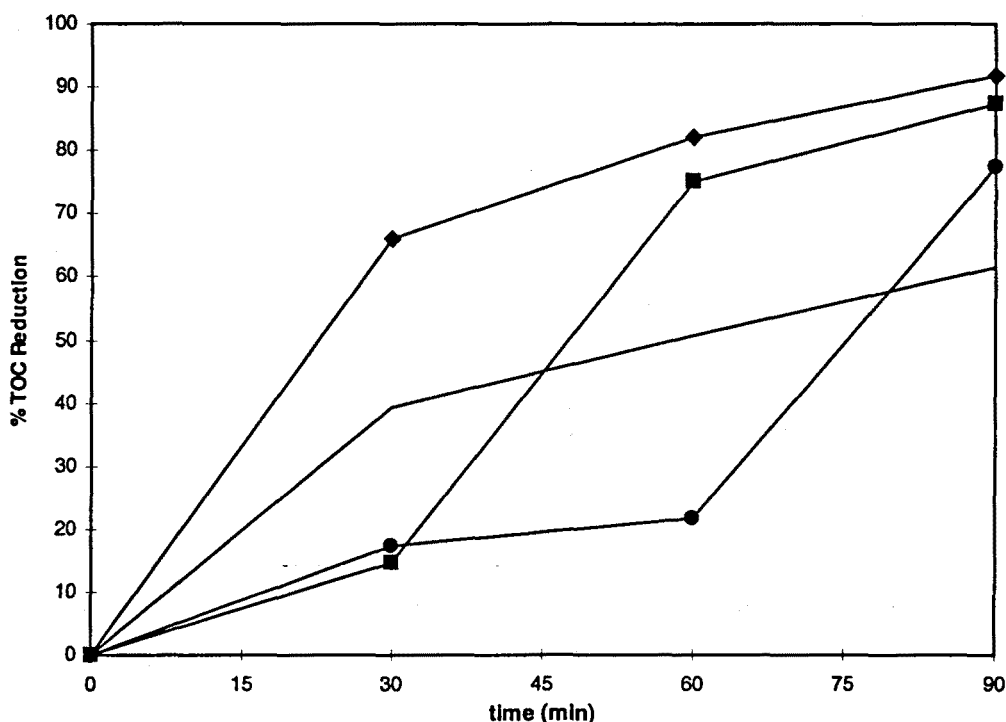


Figure 6. Percentage of TOC reduction vs. time in a 90 minutes treatment of the synthetic 2,4-dichlorophenol sample under several experimental condition: ozonation under UVA irradiation (—); ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II) (◆); one hour stirred 20 mg·L⁻¹ of Fe (II) under irradiation followed for 30 minutes ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II) (●); 30 minutes stirred 20 mg·L⁻¹ of Fe (II) under irradiation followed for one hour ozonation under UVA irradiation in presence of 20 mg·L⁻¹ of Fe (II) (■); pH=3, T=25 °C.

A comparison between the estimated cost of the experiments is summarized in Figure 7. Even the simple addition of iron increases the TOC removal while reducing the estimated cost and, consequently, sequential processes render better results. Both process sequences reach higher TOC removal than ozone/UVA treatment and similar level than the ozone/UVA/Fe(II) process, around 90 %. On the other hand, in both cases the estimated cost is lower, reaching 70 % cost reduction when a pretreatment of one hour is carried out.

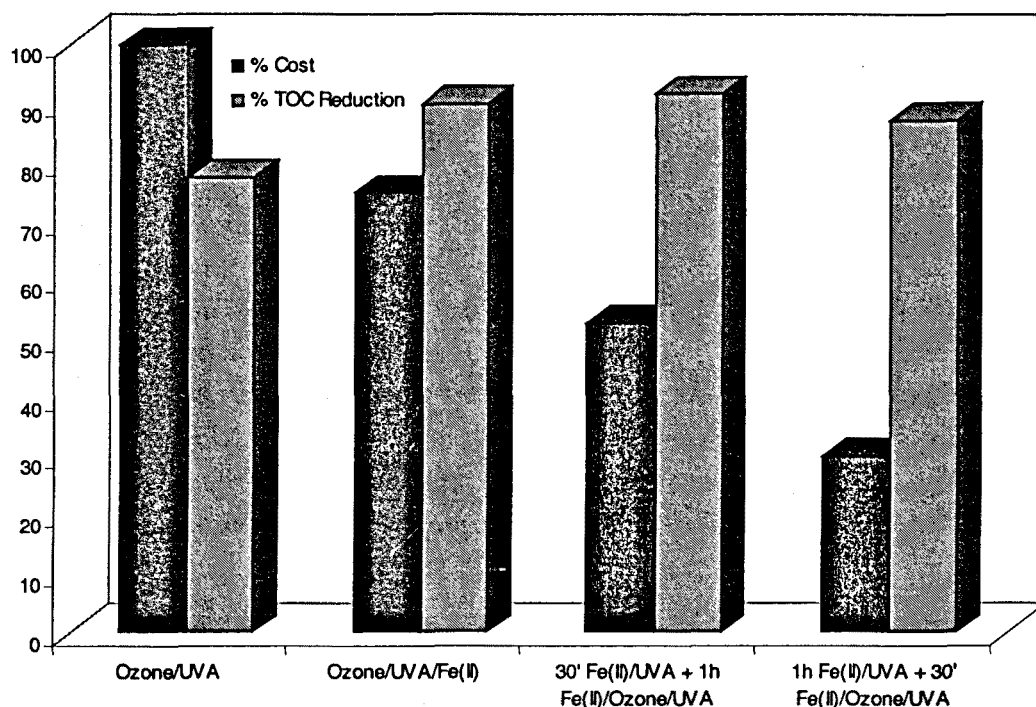


Figure 7. Comparison of the percentage of TOC reduction and estimated costs per kg of TOC removal of various ozonation treatments of the synthetical 2,4-dichlorophenol sample in presence of $20 \text{ mg}\cdot\text{L}^{-1}$ of iron. 90 minutes treatment.

To sum up, similar conclusions that the one obtained with the real bleaching mill wastewater can be derived. Moreover, the results obtained for the synthetic sample are even better than the observed in the real bleaching effluent.

Conclusions

The presence of iron ions in solution when an ozone/UVA treatment of a bleaching mill wastewater is carried out not only generates large rates of TOC removal (90%), but also a 15% of estimated cost reduction. Sequential processes bring noticeable cost reductions. One hour pretreatment under dark condition reach estimate cost reduction of 35% with the same level of TOC removal than ozone/UVA process.

The previous irradiation of the wastewater in presence of iron clearly improves the destruction of the subsequent ozonation step. Maximum estimate cost reduction, 50 %, without decrease in TOC removal is obtained with a 2 hours previous irradiation of the sample in presence of $20 \text{ mg}\cdot\text{L}^{-1}$ of iron, followed by 3 hours of ozonation in presence of iron and irradiation. Longer pretreatment, 3 hours, decreases the cost up to 60 % with a detrimental effect of 10 % decrease in TOC removal. Iron price has not any noticeable effect in the estimate cost reduction.

Similar conclusions were obtained with the synthetic 2,4-dichlorophenol sample investigated. A 70 % cost reduction is obtained when a pretreatment of one hour with 20 ppm of iron under irradiation is followed by 30 minutes of ozonation. In this case TOC removal is 90 % and COD reduction 95 %.

Acknowledgements

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References

1. Yeber MC, Rodríguez J, Baeza J, Freer J, Zaror C, Durán N and Mansilla HD, Toxicity Abatement and Biodegradability Enhancement of Pulp Mill Bleaching Effluent by Advanced Chemical Oxidation, *Water Sci. Technol.* **40**:337-342 (1999).
2. Mansilla HD, Yeber MC, Freer J, Rodríguez J and Baeza J, Homogeneous and Heterogeneous Advanced Oxidation of a Bleaching Effluent from the Pulp and Paper Industry, *Water Sci. Technol.* **35**:273-278 (1997).
3. Yeber MC, Rodríguez J, Freer J, Baeza J, Durán N and Mansilla HD, Advanced Oxidation of a Pulp Mill Bleaching Wastewater, *Chemosphere* **39**:1679-1688 (1999).
4. Sánchez L, Peral J and Domènech X, Aniline degradation by combined photocatalysis and ozonation, *Appl. Catal. B-Environ.* **19**:59-65 (1998).
5. Tanaka K, Abe K and Hisanaga T, Photocatalytic water treatment on immobilized TiO₂ combined with ozonation, *J. Photoch. Photobio. A-Chem.* **101**:85-87 (1996).
6. Muller TS, Sun Z, Kumar G, Itoh K and Murabayashi M, The combination of photocatalysis and ozonolysis as a new approach cleaning 2,4-dichlorophenoxy acetic acid polluted water, *Chemosphere* **36**:2043-2055 (1998).
7. Klare M, Waldner G, Bauer R, Jacobs H and Broekaert JAC, Degradation of nitrogen containing organic compounds by combined photocatalysis and ozonation, *Chemosphere* **38**:2013-2027 (1999).
8. Gratson DA, Nimlos MR and Wolfrum EJ, Photocatalytic Oxidation of Gas-Phase BTEX-Contaminated Waste Streams, *Proceedings Annual Meeting Air Waste Manage. Assoc. Publ.* **88**:11 (1995).
9. Mao H and Smith DW, Influence of ozone application methods on the efficacy of ozone decolorization of pulp mill effluent, *Ozone-Sci. Eng.* **17**:205-236 (1995).
10. Hoigné J, The Chemistry of Ozone in Water, in *Process Technologies for Water Treatment*, ed by Stucki S, Plenum Publishing Corp., New York, (1988).
11. Hoigné J, Organic micropollutants and treatment processes: Kinetic and final effects of ozone and chlorine dioxide, *Sci. Total Environ.* **47**:169-185 (1985).
12. Staehelin J and Hoigné J, Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions, *Environ. Sci. Technol.* **19**:1206-1213 (1985).
13. Bauer R and Fallmann H, The Photo-fenton Oxidation - a cheap and efficient wastewater treatment method, *Res. Chem. Intermediat.* **23**:341-354 (1997).
14. Peyton GR, Smith MA and Peyton BM, Photolytic ozonation for protection and rehabilitation of ground water resources; A mechanistic study, University of Illinois, Water Resources Center, Report n° 206, (1987).
15. Sánchez L, Domènech X, Peral J and Casado J, Solar activated ozonation of phenol and malic acid in contaminated waters, *Submitted in Environ. Sci. Technol.*

16. Tsai TY, Renard JJ and Phillips RB, Formation of polychlorinated phenolic compounds during high chlorine dioxide substitution bleaching, *Tappi J.* **77**:149-157 (1994).
17. Sierka RA and Bryant CW, Biological Treatment of Kraft Wastewater Following Pretreatment of Extraction Waste Stream by Titanium Dioxide and Membranes, in *Photocatalytic Purification and Treatment of Water and Air*, ed by Ollis DF and Al-Ekabi H, Elsevier Science Publishers B.V., Tucson, pp 275-290, (1993).
18. Earl PF and Reeve DW, Chlorinated organic matter in bleached chemical pulp production. Part 6: Chlorinated compounds in effluents, *Tappi J.* **73**:179-183 (1990).
19. Garcia Hortal JA, Vidal T and Colom JF, Características de los efluentes. Blanqueo de pastas papeleras, *Ing. Quim.* 71-82 (1985).
20. Keith LH and Telliard WA, Priority Pollutants: I-a perspective view, *Environ. Sci. Technol.* **13**:416-423 (1979).
21. Tang WZ and Huang CP, 2,4-dichlorophenol oxidation kinetics by Fenton's reagent, *Environ. Technol.* **17**:1371-1378 (1996).
22. Steiert JG, Pignatello JJ and Crawford RL, Degradation of chlorinated phenols by pentachlorophenol degrading bacterium, *Appl. Environ. Microbiol.* **53**:907-910 (1987).
23. Pérez M, Torrades F, Peral J, Lizama C, Bravo C, Casas S, Freer J and Mansilla HD, Multivariate approach to photocatalytic degradation of cellulose bleaching effluent, *Appl. Catal. B-Environ.* **33/2**. 89-96 (2001).
24. Pérez M, Torrades F, Domènech X and Peral J, Removal of organic contaminants in paper pulp effluents by AOP's. Economic study, *Submitted in J. Chem. Technol. Biot.*
25. Logager T, Holcman J, Sehested K and Pedersen T, Oxidation of Ferrous Ions by ozone in acidic solutions, *Inorg. Chem.* **31**:3523-3529 (1992).
26. Pignatello JJ, Dark and photoassisted Fe³⁺catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, *Environ. Sci. Technol.* **26**:944-951 (1992).
27. Safarzadeh-Amiri A, Bolton JR and Cater SR, The use of Iron in Advanced Oxidation Processes, *J. Adv. Oxid. Technol.* **1**:18-26 (1996).
28. Ruppert G, Bauer R and Heisler G, The photo-Fenton reaction - and effective photochemical wastewater treatment process, *J. Photoch. Photobio. A-Chem.* **73**:75-78 (1993).
29. Hislop KA and Bolton JR, The photochemical generation of hydroxyl radicals in the UV-vis/ferrioxalate/H₂O₂ system, *Environ. Sci. Technol.* **33**:3119-3126 (1999).
30. Larson R and Weber E, in *Reaction mechanism in environmental organic chemistry*, ed by Ratón B, p 313-331 (1994).

Paper 5

Removal of organic contaminants in paper pulp treatment effluents by Fenton and Photo-Fenton reactions

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Abstract

The degradation of the organic content of a bleaching kraft mill effluent has been carried out by using Fenton reagent and irradiation providing the conditions needed for the simultaneous occurrence of Fenton and photo-Fenton reactions. The main parameters that govern the complex reactive system, i.e., light intensity, temperature, pH, Fe(II) and H₂O₂ initial concentrations, and O₂ presence in solution have been studied. Concentrations of Fe(II) between 0 and 800 ppm, and H₂O₂ between 0 and 10000 ppm were chosen. Temperatures above 25 °C and up to 70 °C have a beneficial effect on TOC decay rate. The presence of small amounts of O₂ seems to be enough to ensure the reaction progress. The combination of Fenton and photon-Fenton reactions has been proved to be highly effective for the treatment of such a type of wastewaters, and important advantages concerning the application of this combination of reactions arise from the study.

Introduction

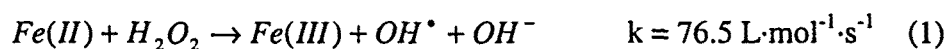
The pulp and paper industry produces large quantities of bleaching effluents that are highly colored and contain large concentrations of organic matter. Most of these contaminants are difficult to eliminate by conventional wastewater treatment processes [1-3].

Nowadays, chemical treatment methods known as Advanced Oxidation Processes (AOPs) have been used for pollutant abatement due to the high oxidative power (2.8 V vs. NHE) of the OH radical, the main reactive species generated by such processes. The most widely known AOPs include: heterogeneous photocatalytic oxidation [4-9], treatment with ozone (often combined with H₂O₂, UVA, or both) [10-16], H₂O₂/UV systems [17,18], Fenton [18-20], and photo-Fenton type reactions [21-23].

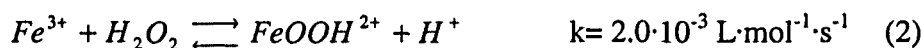
The high electrical energy demand or the consumption of chemical reagents are common problems among all the AOPs [3]. Either generation of O₃ or the production of photons by artificial light sources require an important energy input. However not all photoassisted processes require light with the same wavelength and energy. While direct O₃ or H₂O₂ photolysis need photons of short wavelength (<310 nm), TiO₂ photocatalysis can take advantage of photons of wavelengths up to 380 nm [4], and photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures Fe(III) + H₂O₂ (known as Fenton like reactions [17]) have shown photon absorption up to 550 nm [24,25]

As can be seen, photo-Fenton reaction can be driven with photons of low energy, photons that belong to the visible part of the spectrum. Thus, photo-Fenton processes are a potential cost-reduced AOP that can be run under solar irradiation [23].

In the generally accepted mechanism of Fenton reaction hydroxyl radicals OH· are produced by interaction of H₂O₂ with ferrous salts



Fe(III) can react with H₂O₂ in the so-called Fenton like reaction:





regenerating Fe(II) and thus, supporting the Fenton process [17].

The rate of degradation of the organic pollutants by Fenton reaction could increase when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photoreduction of Fe(III) to Fe(II) ions, a step that produces new OH· radicals and regenerates Fe(II) ions that can further react with more H₂O₂ molecules. The photoreduction of Fe(III) follows the equation:



with Fe(OH)²⁺ being the dominant Fe(III) species in solution at pH 2-3. Recently, it has been proven that the irradiation of Fe(III)+H₂O₂, also called photo-Fenton reaction, enhances the reaction rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to organic matter [25,26]. Absorption of visible light by the complex formed between Fe(III) and H₂O₂ seems to be the cause of formation of such high valence Fe-based oxidants.

In the present paper we have undertaken the study of the oxidation of the organic compounds present in a typical bleaching kraft mill effluent (BKME), by Fenton and Photo-Fenton reactions, in order to establish the efficiency of both AOP for the treatment of such wastewaters. The role that several experimental parameters like pH, temperature, light intensity, and reagent concentration have on the reaction yields has been examined.

Experimental

The effluents used in the present research were supplied by a Spanish paper manufacturer, and obtained from the chlorination step of the bleaching sequence (D₂₀C₈₀)(EO)D₁D₂ applied to kraft paper pulp of *Eucalyptus globulus* (90%) and *Eucalyptus grandis* (10%). In order to reduce the initial level of organic contaminants hydrolysis of the wastewaters with Ca(OH)₂ (pH=12, 1 hour) was carried out.

The rest of the chemicals used were, at least, of reagent grade. Analytical grade hydrogen peroxide and heptahydrated ferrous sulfate were purchased from Panreac and Aldrich, respectively and were used as received. Solutions were prepared with deionized water obtained from a Millipore Mili-Q system.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm³ capacity. The reaction mixture inside the cell, consisting of 100 ml of aqueous sample and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. In the majority of the experiments the temperature was maintained at 25.0±0.1°C. A 6 w Philips black-light fluorescent lamp and a 250 W xenon lamp (Applied Photophysics) were used as light source. The IR fraction of the xenon light beam was removed by the water in the double jacket of the photoreactor. The intensity of the incident light inside the photoreactor, measured employing a uranyl actinometer, was 1.38·10⁻⁹ Einstein·s⁻¹ for the fluorescent lamp and 7.55·10⁻⁸ Einstein· s⁻¹ for the xenon lamp. Neutral density filters were used to modify the light intensity, and a Si photocell was used to measure it.

Total organic carbon (TOC) of initial and irradiated samples was determined with a Shimadzu 5000 TOC analyzer. Color determination of the initial sample was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells, according to standards of the CPPA [27].

Identification of some chemical constituents of the wastewater was attempted by means of GC-MS. A HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector was used. One liter of the sample was filtered with a Speedisk[®] membrane (J.T. Baker) following the EPA 525 procedure. Samples were reconstituted to 100 µL in dichloromethane and 1 µL was injected into the GC. Sample injection was carried out with a 0.6 min of splitless time, at 250 °C. The carrier gas flow rate in the GC was 1.3 mL·min⁻¹. A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with the following dimensions 30 m, 250 µm, 0.25 µm was used. The temperature program used during the GC-MS analysis ramped as follows: 70 °C (3 min), 5°C·min⁻¹ until 270 °C (30 min). The MS analysis was carried out with ionization of electronic impact (70 eV), and the spectra were recorded in the interval 40 – 600 amu. Identifications were carried out with the aid of the data base library WILEY (275,000 spectra) and NIST (130,000 spectra).

Results and discussion

Table 1 summarizes the main features of the wastewater (color, COD and TOC) after alkaline hydrolysis pretreatment.

Table 1. *Initial characterization parameters of the bleaching Kraft mill effluent after hydrolysis pretreatment.*

Parameter	Value
TOC (ppm)	441±8*
COD (mg·L ⁻¹ O ₂)	1384±24*
Color (mg·L ⁻¹ Pt)	197±25*

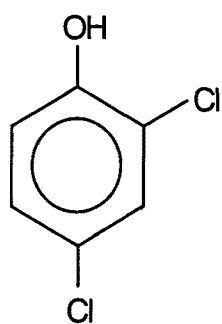
*(n = 4, α = 0.05)

A qualitative analysis of the effluent by GC-MS allows determination of the structure of some low molecular weight compounds present in the effluent. The mass spectra and the identified structures are shown in Table 2 and Figure 1, respectively.

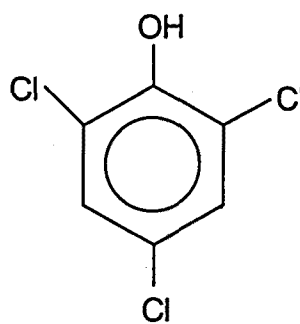
Table 2. *Low molecular weight compounds identified in the bleaching Kraft mill effluent after hydrolysis pretreatment.*

# ^a	rt ^b	mol wt	main fragments	m/z (relative abundance)
1	10.09	162	166 (10), 164 (61), 163 (8), 162 (100), 126 (8), 100 (14), 99 (16), 98 (32), 63 (33), 62 (13), 61 (7)	
2	15.03	196	200 (15), 198 (49), 196 (51), 162 (7), 160 (7), 158 (5), 132 (12), 99 (15), 97 (31)	
3	18.25	192	196 (14), 194 (50), 192 (78), 181 (15), 179 (75), 177 (100), 151 (42), 149 (75), 113 (46)	
4	20.60	226	230 (16), 228 (48), 226 (52), 215 (31), 213 (96), 211 (100), 187 (13), 185 (45), 183 (51), 149 (34), 147 (54), 121 (13), 119 (20)	
5	24.88	260	266 (8), 264 (34), 262 (70), 260 (55), 251 (11), 249 (49), 247 (100), 245 (81), 223 (18), 221 (24), 219 (48), 217 (33), 185 (7), 183 (28), 181 (30)	
6	25.16	256	260 (29), 258 (95), 256 (100), 245 (19), 243 (63), 241 (67), 215 (27), 213 (30), 202 (19), 200 (60), 198 (65), 197 (28), 195 (28)	

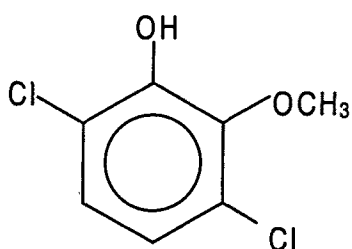
^acompound number. ^bretention time, min.



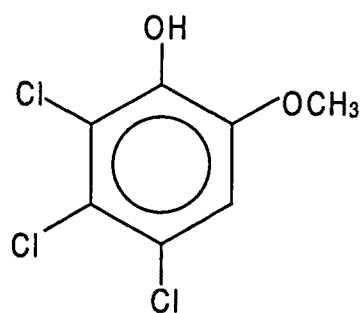
1: 2,4-dichlorophenol



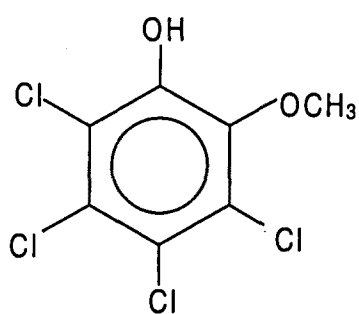
2: 2,4,6-trichlorophenol



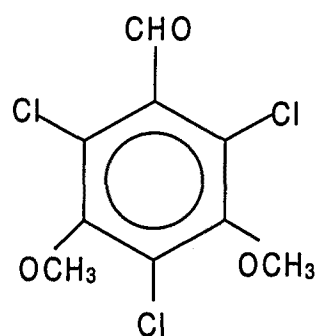
3: 3,6-dichloroguaiacol



4: 4,5,6-trichloroguaiacol



5: tetrachloroguaiacol



6: trichlorosyringol

Figure 1. Structures of some low molecular weight compounds identified by CG-MS analysis of the bleaching effluent after hydrolysis treatment.

All the substances found show a high degree of chlorination. This agrees with structures reported by other authors [28,29]. Also, a large number of unidentified compounds (some of them are long chain carboxylic acids) appear in the chromatogram, although they are not included in table 2. The GC-MS analysis of the effluent after 30 minutes of irradiation and treatment with 450 ppm of Fe(II) and 7500 ppm of H₂O₂, when TOC reduction is around 60 %, indicates the total removal of the low molecular weight chlorinated compounds initially found in the sample. This remarkable finding indicates that, for larger reaction times and higher TOC degradations, the chlorinated compounds should have disappeared. The lack of chlorinated compounds after treatment of this type of wastewater reduces the level of contamination and increases the biodegradability of the effluent [30].

Decrease of organic concentration with time due to oxidative degradation of the paper pulp bleach effluent content by Fenton and Photo-Fenton reaction is shown in Figure 2.

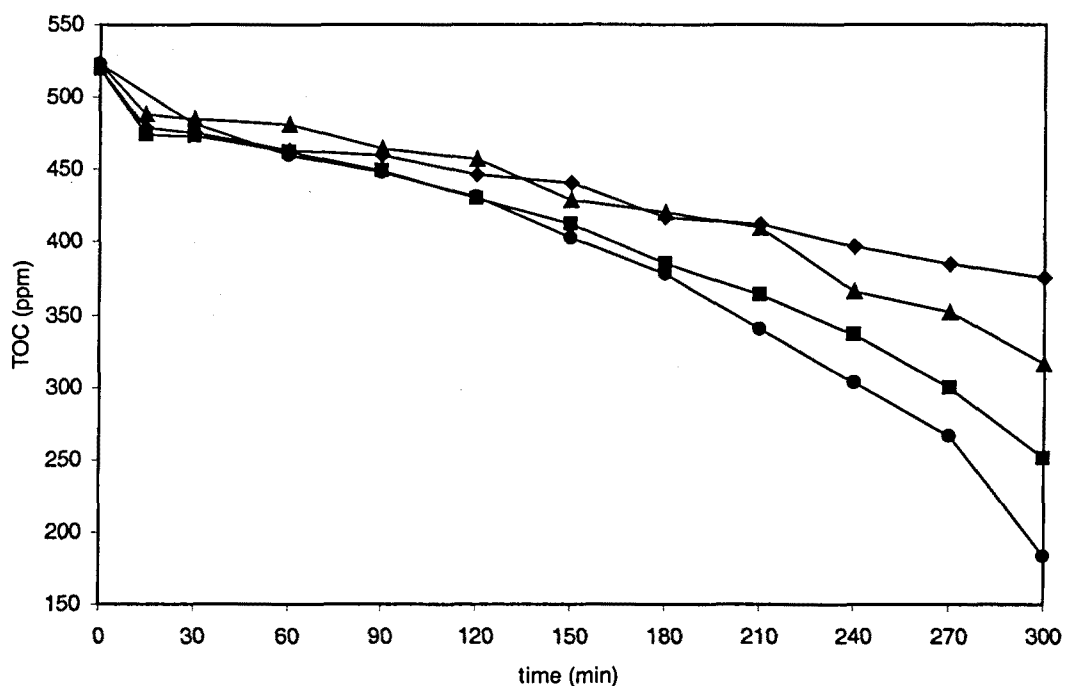


Figure 2. TOC of the paper pulp effluent vs. reaction time for several experimental conditions: 5000 ppm of H₂O₂ in the dark (◆); 5000 ppm of H₂O₂ under UVA irradiation (■); 10000 ppm of H₂O₂ in the dark (▲); 10000 ppm of H₂O₂ under UVA irradiation (●). [Fe(II)]₀=100 ppm, pH=3, T=25 °C.

As can be seen, the increase of H₂O₂ concentration and the use of UVA light improve the reaction rate. Nevertheless, during the first 15 minutes of reaction no significant differences arise between the amount of TOC mineralized in the dark and under illuminated reactions. This fact can be explained by considering that the initial TOC

decrease is mainly due to the dark Fenton reaction, which is faster than Fenton-like [17] or photo-Fenton reactions [24]. With Fe(II) being the limiting reactant, the four experiments should proceed at the same initial reaction rate as long as Fe(II) is available. Under the experimental conditions tested here, Fe(II) consumption takes place in few seconds, producing the majority of TOC decrease observed after 15 minutes of reaction (when the first samples were taken). Thus, for these short reaction times no effect of H₂O₂ concentration or presence of light are noticed.

For long reaction times important differences arise between the four experiments, the best results being obtained in the presence of light, even with the low photon output produced by the black UVA light. The two experiments carried out in the dark are very similar, and only for reaction times above 210 minutes differences between them are detected. Dark reaction rates after Fe(II) consumption are controlled by the Fenton-like process between H₂O₂ and the Fe(III) formed in the first seconds of direct Fenton reaction. The Fenton-like process regenerates Fe(II) (see reactions 2-4) which, in presence of excess H₂O₂ is readily transformed giving Fe(III). Thus, an effective iron cycling takes place, with approximately constant Fe(III) concentration, traces of Fe(II), and a fairly constant oxidant intermediate production. The almost zero order TOC decrease shown in figure 2 for dark experiments agree with these theoretical predictions. Only at the end of the reactions, when a large amount of the initial H₂O₂ has been consumed, the reaction rates begin to differ, being faster the experiment with the larger initial concentration. Pignatello et al. [17] have shown that complete mineralization is hard to achieve under dark Fenton conditions, a fact that is in agreement with the present experimental findings. It is interesting to notice that the rate of TOC removal remains constant in the experiment with 5000 ppm of H₂O₂, while there is a clear increase on reaction rate when for 10000 ppm of H₂O₂ initial concentration. This can be explained by the fact that TOC removal is not directly related to oxidant production rate, being faster as the average oxidation number of carbon in the organic mixture approaches +4, i.e., when the chemical structure of the oxidation intermediates are closer to CO₂.

UVA irradiation improves TOC removal, allowing degradation of more than 60% of initial TOC at 300 minutes. Light can play two different roles that will lead to an improvement of the reaction yields: a) it drives photo-Fenton reaction, producing extra hydroxyl radicals and the recovery of Fe(II) needed in Fenton reaction. The photo-Fenton reaction may involve direct photolysis of ferric ion (equation 5) or photolysis of Fe(III)-peroxy complexes or any of their potential intermediates [25]. b) it can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe(III) and organic compounds, a process that has been well proven for the complexes formed between Fe(III) and the carboxylic acid moiety [31]. Large quantities of

carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate.

The intensity and the wavelengths emitted by the light source are key conditions when trying to describe the participation of the light driven reactions. It is specially interesting, from the application point of view, the possibility of using solar light. The differences in TOC removal when three different light sources are used can be seen in figure 3. The low intensity UVA lamp, emitting a small number of photons, gives de worst results while the sunlight seems to be more effective that the Xe lamp. An assessment of the number of photons with wavelengths below 400 nm coming from the Xe lamp and from the sun and entering the reactor showed a difference of one order of magnitude, with the sun photons being more concentrated. Thus, among the light sources tested, solar light has the largest fraction of photons with the energy needed to drive the photoreactions involved in the present reactive system.

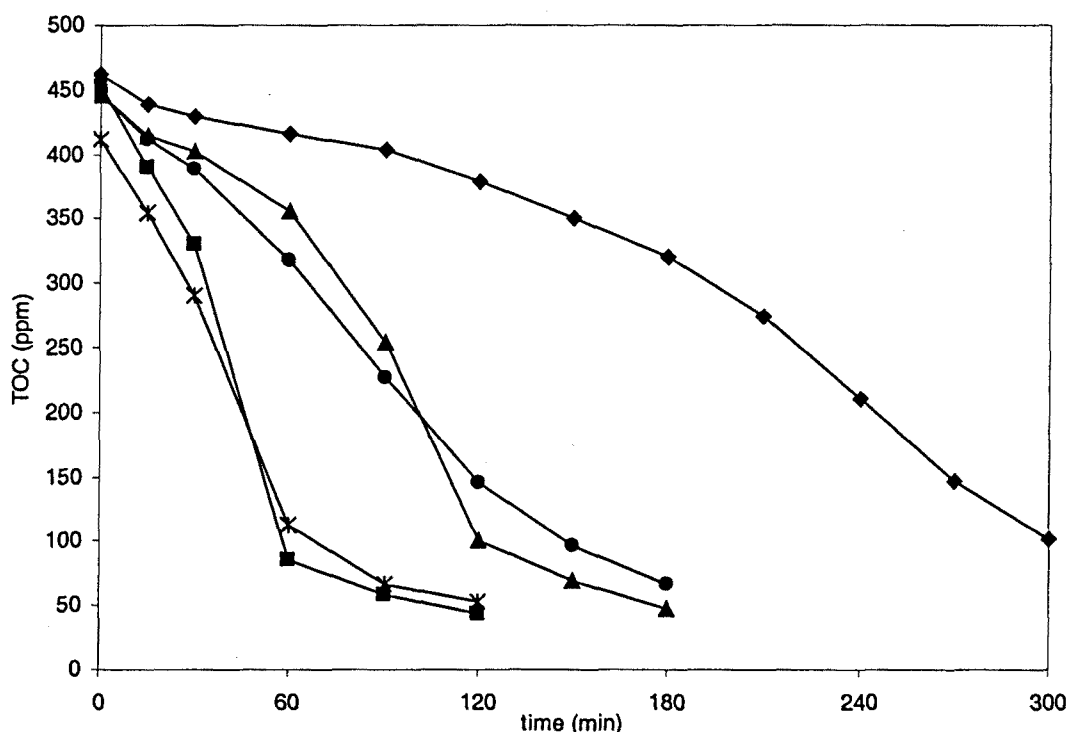


Figure 3. TOC decay vs. reaction time when using different light sources. UVA light and 25 °C (◆); UVA light and 40 °C (●); solar light (■); Xe light and 25 °C (▲); Xe light and 40 °C (*). $[H_2O_2]_0=10000$ ppm, $[Fe(II)]_0=100$ ppm, pH=3.

Nevertheless, figure 3 also shows an interesting dependence of the reaction rate with temperature. In the experiments with UVA light the reaction rate improved when raising the temperature from 25 to 40 °C. The use of Xe light produced the same result. Due to the experimental setup the experiment with solar light was carried out at a single

temperature oscillating between 35 and 40 °C, thus the large reduction of TOC attained in that experiment could be a consequence of both, the number of photons and the temperature.

Experiments with the same light source (Xe lamp) and different light intensities entering the reactor were also conducted. As can be seen in figure 4 no differences exist between the reaction in the dark and the reaction irradiated with approximately the 25 % of the full lamp output. Thus, under such a low photon input the photon-Fenton reaction and any other photochemical pathway taking place are not important in front of the Fenton-like reaction. Intensities of 50 and 80% show an improvement in the reaction yield, especially for long reaction times. The experiment corresponding to 100% intensity involves a large TOC decrease during the first 30-60 minutes of reaction, but experiments with 50, 80 and 100% of the total intensity end up at similar TOC values. All the samples at the end of the experiments became colorless. The shapes of the curves in figure 4 seem to indicate the existence of remaining organic matter in solution (around 50 ppm) that is difficult to eliminate. This is also seen in figure 3 where experiments at higher temperatures (40 °C) are also enclosed.

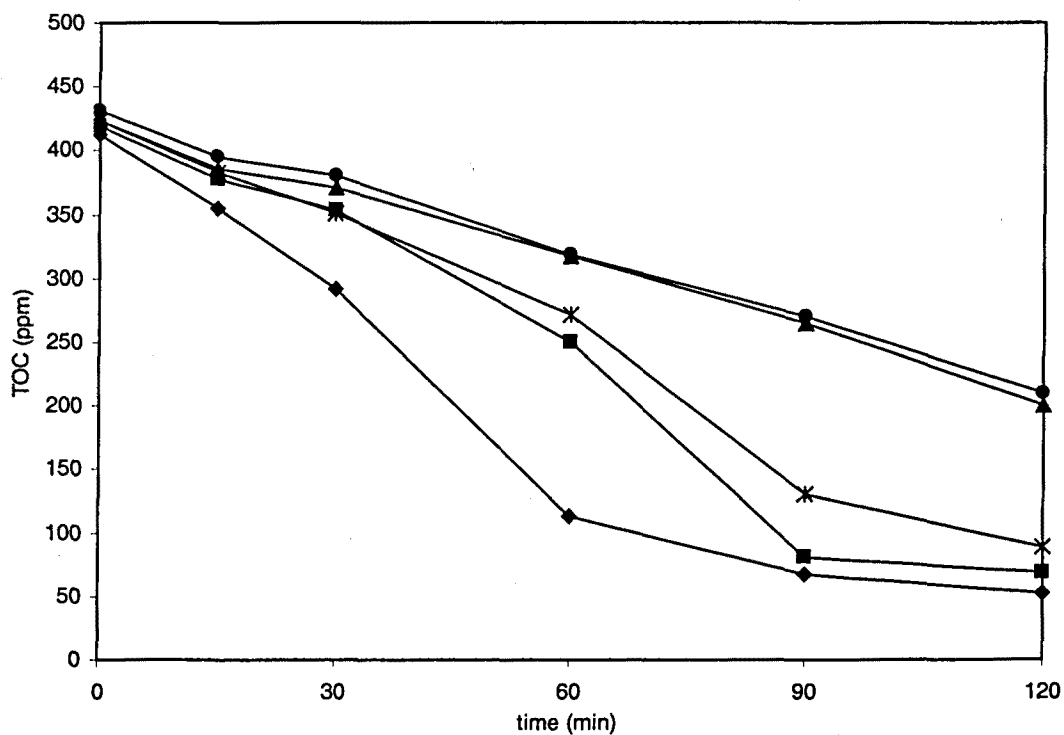


Figure 4. Effect of light intensity on TOC removal. Intensities are measured as a percentage of the total Xe lamp output: 100% (◆); 80% (■); 50% (*); 26% (▲); 0% (●). $[H_2O_2]_0=10000$ ppm, $[Fe(II)]_0=100$ ppm, pH=3, T=25 °C.

In order to check the effect that temperature could have upon the residual TOC a set of experiments (shown in figure 5) at three different temperatures (25, 40 and 70 °C), in the dark and under irradiation of the Xe lamp were carried out. As can be seen, when the experiment was carried out at 70°C, levels of TOC removal over 70 and 80% were attained after just 15 minutes of reaction, both in the dark and under irradiation. Thus, at high temperature the system has similar reaction rates, both in Fenton and Fenton-foto-Fenton conditions. Since the 100 ppm of Fe(II) cannot directly produce enough OH· radicals to account for the level of TOC removal, the acceleration of Fenton reaction with temperature is not the only cause of such an observation. The temperature seems to be assisting alternative ways of H₂O₂ cleavage and OH· formation, or Fe(II) recovery. Blanks experiments showed that neither the irradiation nor the temperature could alone produce noticeable decreases of TOC, the simultaneous presence of Fe(II) and H₂O₂ being always necessary. However, the same persistent organic fraction (50 ppm of TOC) remains in solution even at 70 °C. In all the experiments, the color of the samples at the end was reduced more than 90 %. In any case, temperature is a key parameter that has to be taken into account, especially for those applications where TOC removal rate can be increased by using low cost heat (heat exchangers, co-generation, etc.).

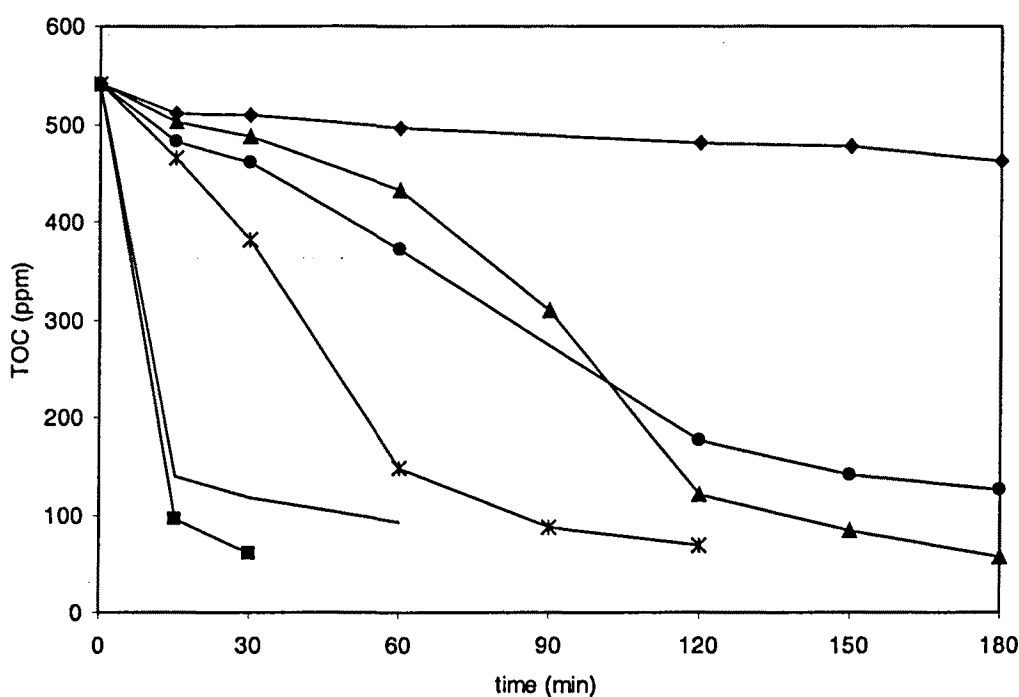


Figure 5. Effect of temperature on TOC removal. 25 °C in the dark (◆); 25 °C under Xe lamp irradiation (▲); 40 °C in the dark (●); 40 °C under Xe lamp irradiation (*); 70 °C in the dark (—); 70 °C under Xe lamp irradiation (■). $[H_2O_2]_0=10000$ ppm, $[Fe(II)]_0=100$ ppm, pH=3.

It is likely that the performance of such a complex reactive system is a function of pH, as expected from equations 1 to 5. However, each reaction has its optimum performance at different pH values: nearly pH independent for the Fenton process [17], optimum at pH 2.8 for the Fenton-like reaction [17], and clearly pH dependent for photo-Fenton reaction [25]. Data concerning TOC degradation of paper mill effluents at several pH is presented in figure 6. As can be seen the fastest removal of TOC takes place at pH=2.8.

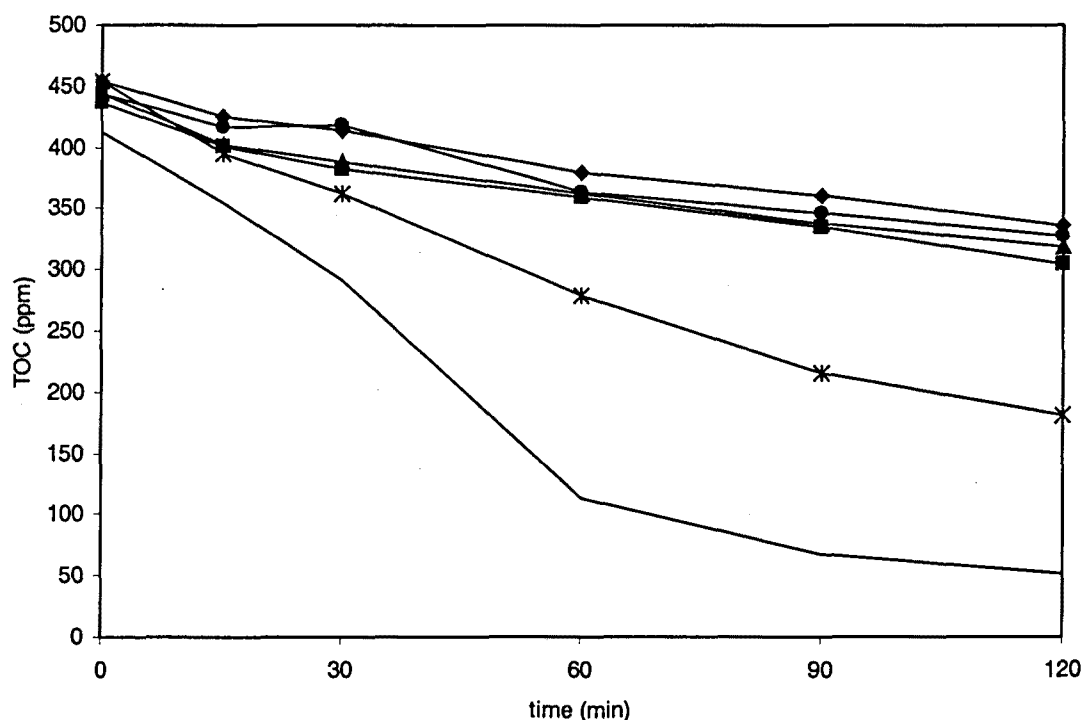


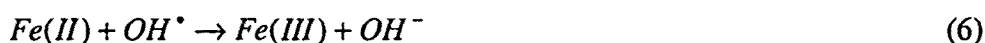
Figure 6. *Effect of pH on TOC reduction. Experiments carried out with the Xe lamp at different pH: 1.5 (◆); 2.8 (—); 5 (*); 8 (▲); 10 (■); 12 (●). $[H_2O_2]_0=10000$ ppm, $[Fe(II)]_0=100$ ppm, $T=25$ °C.*

An acid media (pH=1.5) or a neutral-basic media (pH=8) slow down the process. The low activity detected for high pH values can be explained by the formation and precipitation of $Fe(OH)_3$, a process that hampers the development of photo-Fenton reaction. The decrease of activity for pH values below the optimum is understandable taking into account that Fe (III) forms different species in solution, and the quantum yield of light absorption by Fe(III) is directly depending on the specific species responsible for the absorption.

The main species at pH 2-3, $Fe(OH)^{2+}(H_2O)_5$, is the one with the largest light absorption coefficient and quantum yield for OH^\bullet production, along with Fe(II) regeneration, in the range 280-370 nm [32]. At lower pH, where $Fe^{3+}(H_2O)_6$ is more concentrated, the effectiveness of light absorption, regeneration of Fe(II) and,

eventually, TOC degradation is lower. For larger pH $\text{Fe}(\text{OH})_2^+(\text{H}_2\text{O})_4$ dominates, but the solution becomes unstable with $\text{Fe}(\text{OH})_3$ precipitation [32]. On the other hand, the pH during the reactions always evolved toward the optimal pH value (approximately 3). Larger reductions of solution color have been detected for reactions with pH closer to 3. The experiment carried out at pH=2.8 ended up with a completely colorless solution.

Although Fenton reaction has been widely studied, there is not agreement on the ratio $[\text{H}_2\text{O}_2]/[\text{Fe}(\text{II})]$ that gives the best results. Many authors have reported the use of different ratios of the two reactants. For instance Eisenhauer [33] used 3:1:1 ratios ($\text{H}_2\text{O}_2/\text{Fe}(\text{II})/\text{Phenol}$) for an efficient oxidation of phenol. Sedlak et al. [34] used a 1:4:20 ratio ($\text{H}_2\text{O}_2/\text{Fe}(\text{II})/\text{Chlorobiphenyls}$) in their oxidation experiments. Molar ratios of H_2O_2 as high as 100:1:16 ($\text{H}_2\text{O}_2/\text{Fe}(\text{II})/\text{Chlorophenols}$) were used by Barbeni et al. [35]. Tang et al. [22] reported an 11:1 ratio of $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ for 2,4-Dichlorophenol degradation. Ruppert et al. [20] used a 40:1:4 ratio of $\text{H}_2\text{O}_2/\text{Fe}(\text{II})/4\text{-Chlorophenol}$ in their studies. Bauer et al. [3] used 400:1 molar ratios ($\text{H}_2\text{O}_2/\text{Fe}(\text{II})$) when treating real wastewater. Esplugas et al. [19] used in their experiments ($\text{H}_2\text{O}_2/\text{Fe}(\text{II})$) ratios from 5000:1 to 50:1 ppm, and the results presented so far in this paper were obtained with 100:1:50 ppm ratios ($\text{H}_2\text{O}_2 / \text{Fe}(\text{II}) / \text{Wastewater}$). Large excess of H_2O_2 or Fe^{2+} might be detrimental, since these species can react with some of the intermediates like OH^\bullet , responsible of the direct oxidation of the organic load:



precluding the extent of mineralization. Thus, in order to check the effect that different reagent ratios have on the reactions, experiments with several $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ ratios were conducted. Figure 7 shows that, in general, large initial quantities of iron in solution produces increasing rates of degradation. Although during the first minutes the reaction with more $\text{Fe}(\text{II})$ proceeds at a faster rate, at long reaction times the experiment with 800 ppm of $\text{Fe}(\text{II})$ produces a TOC decay that is slightly minor than the one obtained with 400 ppm. This change on behavior with time can be explained by taking into account that Fenton reaction, which is completed after few seconds, benefits from a larger $\text{Fe}(\text{II})$ load, while detrimental reactions like 6 and 7, due to the low concentration of OH^\bullet , need more time to manifest, and their effects only appear for long enough reaction times, when they compete with slower reactions as Fenton-like, photo-Fenton, photochemical processes, etc.

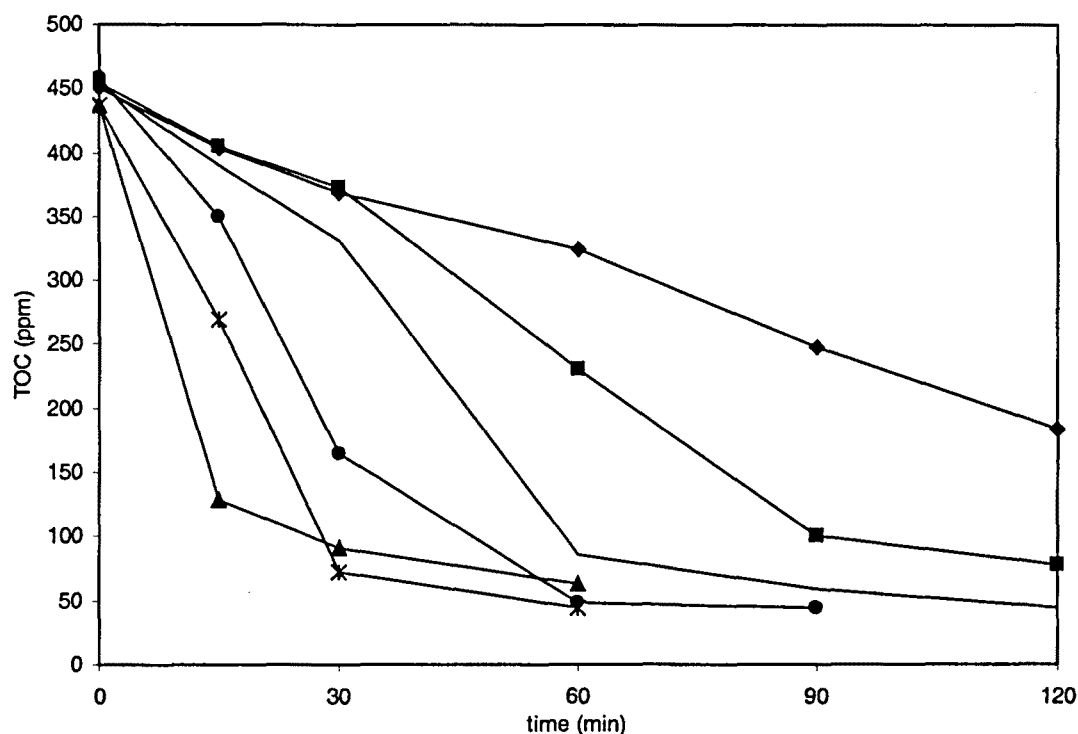


Figure 7. Effect of Fe(II) doses on TOC reduction. The initial concentrations of Fe(II) were as follows: 25 ppm (◆); 50 ppm (■); 100 ppm (—); 200 ppm (●); 400 ppm (*); 800 ppm (▲). $[H_2O_2]_0 = 10000$ ppm, $pH = 3$, $T = 25$ °C.

On the other hand, the use of large quantities of Fe in solution has a negative effect from the applied point of view, since it implies the need of an additional treatment step for Fe removal. Figure 8 contains data concerning experiment with several initial H_2O_2 doses. In this case it is clear that increasing amounts of H_2O_2 lead to larger TOC removal, with no detrimental effects detected for the highest H_2O_2 . Nevertheless, the small difference between the TOC removal attained with 5000 and 10000 ppm of H_2O_2 indicates that improvements of reaction rate may not be worth the large loads of oxidant expended. It is interesting to note that, for the least H_2O_2 concentrated experiments the TOC removal slows down to few ppm per hour, showing that, even for Fenton-photo-Fenton systems large enough concentrations of H_2O_2 are essential. In both sets of experiments (figures 7 and 8) the color was totally eliminated at the end of the reactions.

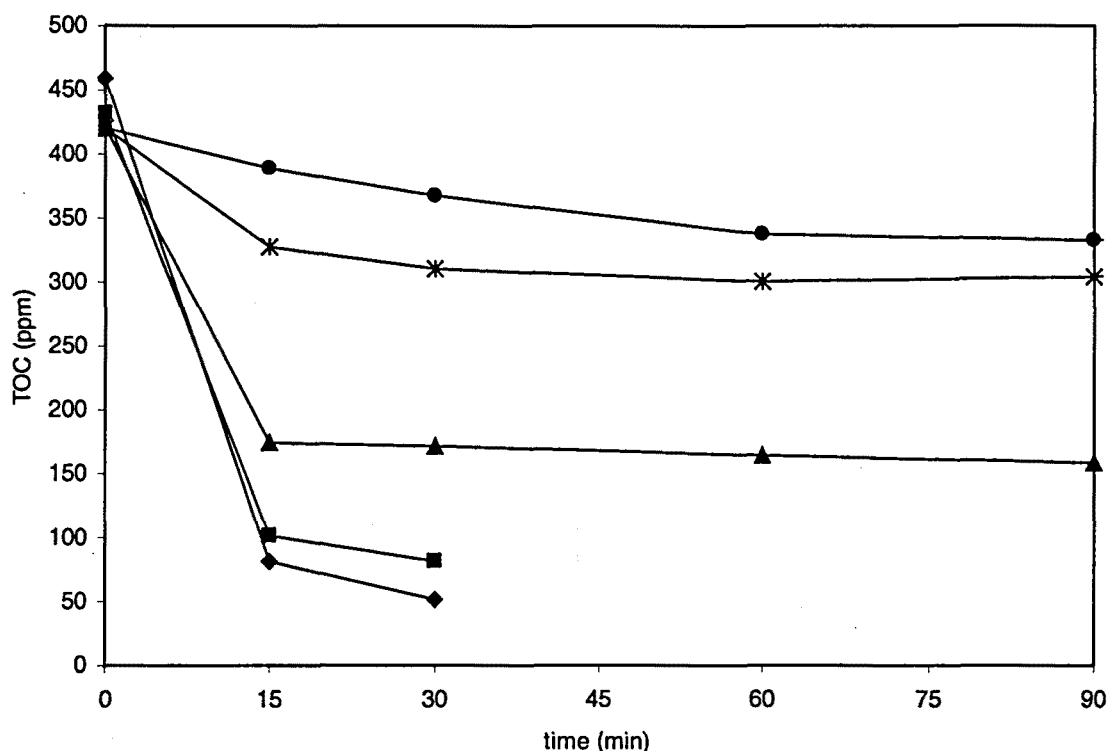
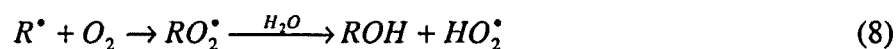


Figure 8. Effect of H_2O_2 doses on TOC reduction. The initial concentrations of H_2O_2 were as follows: 10000 ppm (◆); 5000 ppm (■); 2500 ppm (▲); 1000 ppm (*); 0 ppm (●). $[Fe(II)]_0=100$ ppm, $pH=3$, $T=70$ °C.

It has been reported that bubbling of molecular oxygen can help the mineralization reactions by incorporating the new oxidant into the complex reaction mechanism of the Fenton-photo-Fenton systems [36]. O_2 consumption can be due to three different reasons [17]: a) O_2 reacts with intermediate organoradicals [37] to form photolabile Fe(III) complexes, thus promoting overall mineralization; b) the reaction between O_2 and the intermediate organoradicals generates H_2O_2 by the “Dorfman” mechanism:



with Fe(II) acting as electron source [37]; c) the intermediate hydroperoxides and organoperoxides serve to oxidize Fe(II) to Fe(III):



which is photoactive. In any case, direct oxidation of Fe^{2+} by O_2 (autoxidation) is too slow in acidic solution to be important [17].

Experiments were carried out in order to check the effect of O₂ bubbling through the solutions. Figure 9 shows that no appreciable improvements are obtained when the oxidations were performed under an O₂ rich atmosphere.

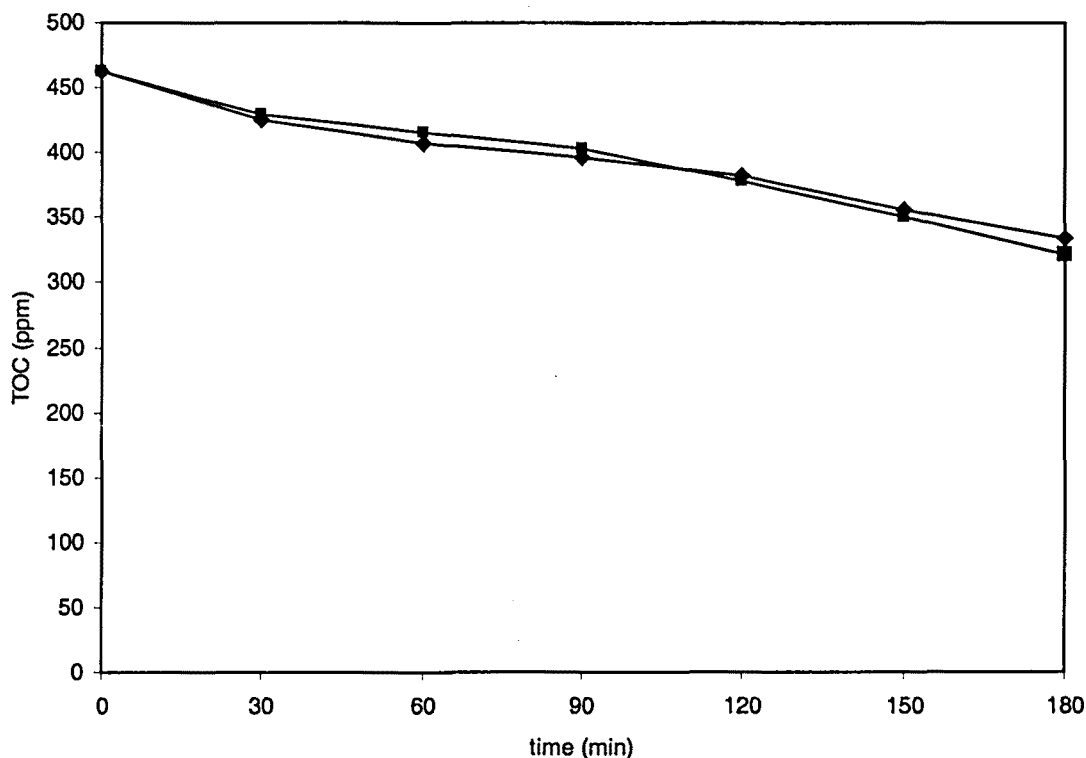


Figure 9. *Effect of O₂ bubbling on TOC reduction: in absence of air bubbling (■); in presence of air bubbling (◆). [H₂O₂]₀=10000 ppm, [Fe(II)]₀=100 ppm, pH=3, T=25 °C.*

Two tentative explanations are given for this experimental behavior: a) Fenton, Fenton-like, and photo-Fenton reactions are catalyzed decomposition of H₂O₂ to O₂ and H₂O. Thus, O₂ is always present in the system and air bubbling do not affect its concentration; b) the solutions are O₂ saturated, even for the lowest O₂ flow rates.

Conclusions

The degradation of the organic content of a bleaching Kraft mill effluent has been successfully carried out by simultaneously applying Fenton and photo-Fenton conditions. From the data it is clear that, under the specific experimental conditions of the work, Fenton reaction applies during the very first seconds, while photo-Fenton, Fenton-like, and other potential photochemical processes are only important after several minutes. Irradiations were done with different light sources, being more effective those with larger photon output below 400 nm. Solar light irradiation turns out

to be particularly efficient. Temperature is a key parameter, markedly increasing reaction rates, although a residual TOC persisted and could not be eliminated even at high temperature. pH=3 is the optimal value for the simultaneous concurrence of all reactions. Initial concentrations of Fe(II) in solution above 400 ppm were found to be detrimental, while up to the values tested in this work the reactivity was larger the higher the concentration of H₂O₂. Finally, the bubbling of O₂ through the solutions does not improve the reaction yields, suggesting that for the studied systems and under the specified conditions O₂ saturation is always achieved. The irradiation of the reaction of mineralization of Kraft paper mill effluents with Fenton reagent and the occurrence of photo-Fenton and photochemical reactions has clear advantages from the applied point of view, advantages that are outlined through the text.

Acknowledgements

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References

1. Sierka, R.A., Bryant, C.W., *Photocatalytic Purification and Treatment of Water and Air*, Ollis, D.F., and Al-Ekabi, H., Ed., (1993)275.
2. Tsai, T.Y., Renard, J.J., Phillips, R.B., *Tappi J.*, 77(1994)149.
3. Bauer, R., Fallmann, H., *Res.Chem.Intermed.*, 23(1997)341.
4. Hoffmann, M.R., Martin S.T., Choi, W., Bahnemann, D.W., *Chem.Rev.*, 95(1995)69.
5. Ollis, D.F., in *Photochemical Conversion and Storage of Solar Energy*, Pelizzetti, E., and Schiavello, M., Ed., Kluwer, Dordrecht,1991.
6. Linsebigler, A.L., Lu, G., Yates, J.T., *Chem. Rev.*, 95(1995)735.
7. Fox, M.A., Dulay, M.T., *Chem.Rev.*, 93 (1993) 341.
8. Pérez, M., Torrades, F., García Hortal, J.A., Domènech, X., Peral, J., *J. Photochem. Photobiol. A: Chem.*, 109(1997)281.
9. Mills, A., Le Hunte, S., *J. Photochem. Photobiol. A: Chem.*, 108(1997)1.
10. Saunamäki, R., Sorvari, J., *Nordic Pulp and Paper Research Journal*, 3(1992) 113.
11. Sánchez, L., Peral, J., Domènech, X., *App.Catal. B: Environm.*, 19(1998)59.
12. Tanaka, K., Abe, K., Sheng, C.Y., Hisanaga, T., *Environ. Sci. Technol.*, 26(1992) 2534.
13. Tanaka, K., Abe, K., Hisanaga, T., *J. Photochem. Photobiol. A: Chem.*, 101(1996) 85.
14. Muller, T.S., Sun, Z., Kumar, G., Itoh, K., Murabayashi, M., *Chemosphere*, 36(1998)2043.
15. Klare, M., Waldner, G., Bauer, R., Jacobs, H., Broekaert, J.A.C., *Chemosphere*, 38(1999)2013.
16. Logager, T., Holcman, J., Sehested, K., Pedersen, *Inorg. Chem.*, 31(1992)3523.
17. Pignatello, J., *Environ. Sci. Technol.*, 26(1992)944.
18. Peyton, G.R., in *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, Lewis Publishers, Chelsea,1990, p. 313.
19. Chamarro, E., Marco, A., Esplugas, S., *Water Research*, 35(2001)1995.
20. Ruppert, G., Bauer, R., Heisler, G., *J. Photochem. Photobiol. A: Chem.*, 73(1993)75.
21. Kiwi, J., Pulgarin, C., Peringer, P., *Appl. Catal. B: Environm.*, 3(1994)335.
22. Tang, W.Z., Huang, C.P., *Environ. Technol.*, 17(1996)1371.
23. Safarzadeh-Amiri, A., Bolton, J.R., Cater, S.R., *J. Advan. Oxid. Technol.*, 1(1996)1.
24. Sun, Y., Pignatello, J.J., *Environ.Sci. Technol.*, 27(1993)304.
25. Pignatello, J.J., Liu, D., Huston, P., *Environ. Sci. Technol.*, 33(1999)1832.
26. Bossmann, S.H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E.P., Payawan, L., Straub, M., Wörner, M., Braun, A.M., *J. Phys. Chem.*, 102(1998)5542.
27. Canadian Pulp and Paper Association, Standard H.5, 1991.
28. Pérez, M., Torrades, F., Peral, J., Lizama, C., Bravo, C., Casas, S., Freer, J., Mansilla H.D., *Appl. Catal. B: Environm.*, 33/2(2001)89.
29. Kringtad, K.P., Lindström, K., *Environ. Sci. Technol.*, 18(1984)236.
30. Yeber, M.C., Freer, J., Martínez, M., Mansilla, H.D., *Chemosphere*, 41(2000)1257.
31. Hislop, K.A., Bolton, J.R., *Environ. Sci. Technol.*, 33(1999)3119.
32. Benkelberg, H-J., Warneck, P., *J. Phys. Chem.*, 99(1995)5214.

33. Eisenhauer H.R., *J. Water Pollution Control Federation*, 36(1964)1116.
34. Sedlak, D.L., Andren, A.W., *Environ. Sci. Technol.*, 25(1991)777.
35. Barbeni, M., Minero, C., Pelizzetti, E., Borgarello, E., and Serpone, N., *Chemosphere*, 16(1987)2225.
36. Utset, B., Garcia, J., Casado, J., Domènech, X., Peral, J., *Chemosphere*, 41(2000)1187.
37. Kunai, A., Hata, S., Ito, S., Sasaki, K., *J. Am. Chem. Soc.*, 108(1986)6012.

Paper 6

Experimental design of Fenton and Photo-Fenton reaction of cellulose bleaching effluent

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Abstract

Multivariate experimental design was applied to the treatment of a cellulose conventional bleaching effluent in order to evaluate the use of the Fenton reagent under solar light irradiation. The effluent was characterized by the general parameters TOC, COD and color, and it was analyzed for chlorinated low molecular weight compounds using GC-MS. The main parameters that govern the complex reactive system: Fe(II) and H₂O₂ initial concentration, and temperature were simultaneously studied. Factorial experimental design allowed to assign the weight of each variable in the TOC removal after 15 minutes of reaction. Temperature had an important effect in the organic matter degradation, especially when the ratio of Fenton reagents was not properly chosen. Fenton reagent under solar irradiation proved to be highly effective for these types of wastewaters. A 90% TOC reduction was achieved in only 15 minutes of treatment. In addition, the GC-MS analysis showed the elimination of the chlorinated organic compounds initially present in the studied bleaching effluents.

keywords: Cellulose bleaching effluent, chlorinated phenols, experimental design, Fenton, Fenton-like and Photo-Fenton reactions, solar irradiation.

Introduction

Wastewaters generated by the bleaching of paper pulp contain large concentrations of organic matter [1]. The chlorinated phenols and polyphenolic compounds present in these types of effluents have been a source of environmental concern due to their toxicity, bio-accumulation and carcinogenic potential [2,3]. This carcinogenic potential is higher with an increase in the number of chlorine atoms per molecule [4,5].

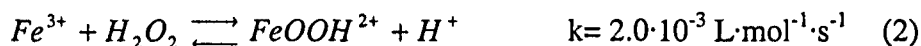
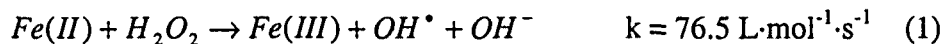
Worldwide kraft mill industry uses two approaches to comply with increasingly strict pollution control regulations. The first approach employs in-plant process modifications such as extended delignification and substitution of elemental chlorine in the bleaching stage. When molecular chlorine is replaced by chlorine dioxide in the ECF (Elemental Chlorine Free) bleaching process, the amount of chlorinated phenols formed decreases [3]. However, small amounts of chlorinated phenols remain in solution even in a dioxide chlorine ECF bleaching sequence.

The second approach involves the treatment of wastewaters by physical-chemical processes including chemical oxidation (i.e. ozone). Also, both aerobic and anaerobic biological treatment schemes have been applied to individual process and total plant wastewaters. However, in the presence of toxic or recalcitrant compounds the biological treatments may be inhibited or simply the microbiological flora destroyed.

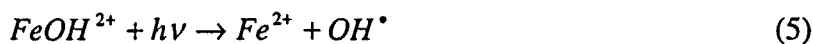
Recently, advanced oxidation processes (AOPs) have been applied in order to reduce the organic load of cellulose mill effluents. AOPs utilize the high oxidative power (2.8 V vs. NHE) of the OH^\bullet radical, the main reactive species generated by such processes. The most widely known AOPs include: heterogeneous photocatalytic oxidation [6-15], treatment with ozone (often combined with H_2O_2 , UVA, or both and even with heterogeneous photocatalytic processes) [16-27], Fenton [28-31] and Photo-Fenton type reactions [31-34].

High electrical energy demand or excessive consumption of chemical reagents are common problems among all AOPs [35]. However, not all photoassisted processes require light with the same wavelength and energy. While direct O_3 or H_2O_2 photolysis need photons of short wavelength (<310 nm), TiO_2 photocatalysis can take advantage of photon wavelengths up to 380 nm [6], and photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures $\text{Fe(III)} + \text{H}_2\text{O}_2$ (known as Fenton like reactions [36]) have shown photon absorption up to 550 nm [37,38]. Thus, photo-Fenton reaction can be driven with low-energy photons in the visible part of the spectrum. Thus, Photo-Fenton processes are a potentially low-cost AOP that can be run under solar irradiation [34].

In the generally accepted mechanism of Fenton reaction hydroxyl radicals OH^\bullet are produced by interaction of H_2O_2 with ferrous salts (reaction (1)). Additionally, Fe(III) can react with H_2O_2 in the so-called Fenton like reaction (reactions (2)-(4)) regenerating Fe(II) and thus, supporting the Fenton process [36]:



The rate of degradation of the organic pollutants by Fenton reaction could increase when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photoreduction of Fe(III) to Fe(II) ions, a step that produces new OH^\bullet radicals and regenerates Fe(II) ions that can further react with more H_2O_2 molecules. The photoreduction of Fe(III) follows the equation:



with Fe(OH)^{2+} being the dominant Fe(III) species in solution at pH 2-3. Recently, it has been proven that the irradiation of $\text{Fe(III)} + \text{H}_2\text{O}_2$, also called Fenton-like reaction, enhances the reaction rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to organic matter [38,39]. Absorption of visible light by the complex formed between Fe(III) and H_2O_2 seems to be the cause of formation of such high valence Fe-based oxidants.

The purpose of this study is to apply Fenton, Fenton-like and Photo-Fenton reactions to reduce the amount of chlorinated compounds and organic contaminants in an industrial wastewater. The effluents are produced in the $\text{D}_{22}\text{C}_{78}$ stage (22% of ClO_2 substitution) of the conventional bleaching sequence of kraft pulp coming from 90% of *Eucalyptus globulus* and 10 % of *Eucalyptus grandis*. Oxygen delignification (O) previous to the chlorine bleaching stage ($\text{D}_{22}\text{C}_{78}$) was applied in order to lower the level of contamination. The effluents were chosen because their contaminant load is suitable for treatment and compliance with environmental legislation [40].

Multivariate analysis is an important tool for obtaining valuable and statistically significant models of a phenomena by performing a minimal number of well-chosen experiments. With a determined number of assays information regarding the importance

of each variable and the interaction effects between them can be obtained. Using this technique, it is possible to assess the conditions that will yield the most desirable response. Applications of this statistical methodology have been reported for pulp mill effluent treatment with heterogeneous photocatalytic oxidation, [15] ozone [41] and in the Fenton reaction of industrial wastewaters containing aromatic amines [42]. In the present paper multivariate analysis was used to evaluate the importance of Fenton reagent concentration, and temperature in TOC removal.

GC-MS analyses of the effluent were performed throughout the course of the reaction to determine levels of chlorophenol compounds. Even though chlorophenols do not constitute the major fraction of the compounds contained in the effluent, it is necessary to eliminate or reduce them due to their high toxicity and the risk they pose to the aquatic environment.

Experimental

The effluents used in the present research were obtained from the chlorination step of the conventional bleaching sequence O(D₂₂C₇₈)(EO)D₁D₂ applied to Kraft paper pulp of *Eucalyptus globulus* (90%) and *Eucalyptus grandis* (10%), that was supplied by a Spanish paper manufacturer. The effluent was stored at -4°C and used as received.

The rest of the chemicals used were, at least, of reagent grade. Analytical grade hydrogen peroxide and heptahydrated ferrous sulfate were purchased from Panreac and Aldrich, respectively, and were used as received. Solutions were prepared with deionized water obtained from a Millipore Mili-Q system.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm³ capacity. The reaction mixture inside the cell, consisting of 100 ml of organic effluent and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. Temperature was maintained at ±0.1°C. Solar irradiation was used as light source. An assessment of the light energy below 400 nm entering the reactor gave 5·10⁻³ W·cm⁻² (with a presumably larger photon input below 500 nm).

Total organic carbon (TOC) of initial and irradiated samples was determined with a Shimadzu 5000 TOC analyzer. Color determination was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells and referenced to a Pt-Co standard solution, according to standard H.5 of the CPPA [43]. Chemical Oxygen Demand (COD) was determined by standardized methodology (n° 5220 C) [44].

For the analysis of low molecular weight compounds dissolved in the effluent, a HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector was used. The GC-MS analysis was carried out with ionization of electronic impact, 70 eV, the spectra were recorded in the interval 40 – 600 amu. One liter of the sample was filtered with Speedisk[®] membrane (J.T. Baker) following the EPA 525 procedure. Samples were reconstituted to 100 μ L in dichloromethane and 1 μ L was injected in the GC. Identifications were carried out with the aid of the data base library WILEY (275,000 spectra) and NIST (130,000 spectra) and with a customized database generated in our laboratory.

A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with the following dimensions 30 m, 250 μ m, 0.25 μ m was used. The carrier gas flow rate in the GC was 1.3 mL \cdot min⁻¹. The sample injection was carried out with a 0.6 min of splitless time, at 250 °C. The temperature program used during the GC-MS analysis ramped as follows: 70 °C (3 min), 5°C \cdot min⁻¹ until 270 °C (30 min).

Results and discussion

Table 1 summarizes the main features of the effluent used in this study. The magnitudes reveal high color, COD and TOC. The Fenton and Photo-Fenton reactions were applied to the cellulose bleaching effluent in order to reduce these initial parameters. The removal of organochlorinated compounds and TOC to yield a regulation-compliant effluent is the main goal of this study. Should the treatment not yield regulation-compliant effluents, it is hoped that they will, at minimum, be made amenable to biological treatment.

Table 1. *Initial characterization parameters of the bleaching Kraft mill effluent.*

Parameter	Value
TOC (ppm)	537 \pm 9*
pH	1.74 \pm 0.08*
COD (mg \cdot L ⁻¹ O ₂)	1250.5 \pm 7*
Color (mg \cdot L ⁻¹ Pt)	649 \pm 53*

*(n = 4, α = 0.05)

As expected from equations 1 to 5 the complex reactive system is a pH dependent processes. However, each reaction has its optimum performance at different pH values: nearly pH independent for the Fenton process [36], optimum at pH 2.8 for the Fenton-like reaction [36], and clearly pH dependent for photo-Fenton reaction [38]. Data concerning TOC degradation of paper mill effluents at several pH levels shows that the

faster removal of TOC takes place at pH=2.8 [31]. A very acid media or a neutral-basic media slows down the process. The low activity detected for high pH values can be explained by the formation and precipitation of $\text{Fe}(\text{OH})_3$, a process that hampers the development of photo-Fenton reaction. The decrease of activity for pH values below the optimum is understandable taking into account that Fe (III) forms different complex species in solution, and the quantum yield of light absorption by Fe(III) is directly depending on the specific specie responsible for the absorption.

Safarzadeh-Amiri, A., et al. [34] studied the predominant iron species in several pH ranges. The main species at pH 2-3, $\text{Fe}(\text{OH})^{2+}(\text{H}_2\text{O})_5$, is the one with the largest light absorption coefficient and quantum yield for OH^\bullet production, along with the larger Fe(II) regeneration ability, in the range 280-370 nm [45]. At lower pH, where $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ is more concentrated, the effectiveness of light absorption, regeneration of Fe(II) and, eventually, TOC degradation is lower. For larger pH $\text{Fe}(\text{OH})_2^+(\text{H}_2\text{O})_4$ dominates, but the solution becomes unstable with $\text{Fe}(\text{OH})_3$ precipitation [45]. On the other hand, the pH during the reactions evolved toward the optimal pH value (approximately 3) [31]. Thus, pH 3 was the pH used in all the experiments presented in this study.

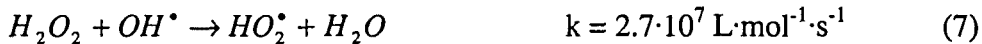
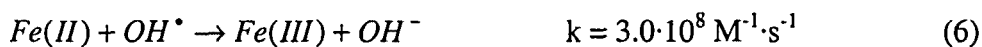
Pignatello et al. [36] have shown that complete mineralization is hard to achieve under dark Fenton conditions, a fact that is in agreement with previous experimental findings of our research group [31]. It is also known that light can play two different roles that will lead to an improvement of the reaction yields: a) it drives photo-Fenton reaction, producing extra hydroxyl radicals and the recovery of Fe(II) needed in Fenton reaction. The photo-Fenton reaction may involve direct photolysis of ferric ion (equation 5) or photolysis of Fe(III)-peroxy complexes or any of their potential intermediates [38]. b) it can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe(III) and organic compounds, a process that has been well proven for the complexes formed between Fe(III) and the carboxylic acid moiety [46]. Large quantities of carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate. Previous reported works [31] show that among the light sources tested, solar light has the largest fraction of photons with the energy needed to drive the photoreactions involved in the reactive system. This fact makes advisable to use solar light as a source of light.

This paper studies the effect of varying temperature and reagent (Fe(II) and H_2O_2) concentration in a complex system involving Fenton, Fenton-like and Photo-Fenton reaction for the degradation of organic matter dissolved in a cellulose bleaching effluent. The reaction was carried out at room temperature and at progressively increasing temperatures up to the maximum value of 70°C. The natural temperature of the effluent depends on the kind of industrial process. This range of variation was

chosen because the common practice of using heat exchangers and co-generation in the paper and pulp industries could increase the temperature of wastewaters with very little cost.

Variations in the magnitude of the Fenton reagent concentration (50 to 450 gL⁻¹ of Fe (II) and 10³ to 10⁴ gL⁻¹ of H₂O₂) were tested. The amounts of Fe (II) and H₂O₂ used were in the range normally reported for Fenton and photo-Fenton systems applied to the degradation of pure compounds or complex effluents. Molar ratios of H₂O₂ as high as 100:1:16 (H₂O₂/Fe(II)/Chlorophenols) were used by Barbeni et al. [47]. Tang et al. [33] reported a 11:1 ratio of H₂O₂/Fe(II) for 2,4-Dichlorofenol degradation. Ruppert et al. [30] used a 40:1:4 ratio of H₂O₂/Fe(II)/4-Chlorofenol in their studies. Bauer et al. [35] used 400:1 molar ratios (H₂O₂/Fe(II)) when treating real wastewater. Esplugas et al. [29] used from 5000:1 to 50:1 ppm ratios (H₂O₂/Fe(II)) in their experiments, and previous results reported from our research group involved 100:1:50 ppm ratios (H₂O₂ / Fe(II)/ Wastewater) [31].

One factor that must be considered is that an excess of H₂O₂ or Fe²⁺ might be detrimental since these species can react with some of the intermediates like the OH radical, responsible of the direct oxidation of the organic load, as follows:



Previous works with Kraft bleaching effluents that have similar contaminant loads and characteristics have shown that a detrimental behavior is observed when iron concentration is above 400 ppm [31]. Consequently, in order to check the effect that different reagent ratios have on the reactions, experiments with several ratios of H₂O₂/Fe(II) were conducted following the experimental design.

A factorial experimental design (2³) was carried out considering low and high levels for Temperature (30-70°C), Fe (II) (50-450 g·L⁻¹) and H₂O₂ (10³-10⁴ g·L⁻¹). Table 2 shows the description of the experiments and the relation between codified and real experimental values. Low and high levels are denoted by (-1), (+1) respectively, the central points as (0). From the values shown in Table 2 and assuming a second order polynomial model, at least 13 experiments must be carried out to solve the matrix (including the interaction effects between variables) and the error evaluation.

The matrix was resolved using the software FATORIAL [48]. The percentage of TOC present after only 15 minutes of reaction was used as the response factor. The coefficients of the quadratic model in the polynomial expression were calculated by

multiple regression analysis. These coefficients represent the weight of each variable, the quadratic effect and the first-order interaction between the coded variables.

Table 2. *Factorial experimental design of the wastewaters treated by Fenton and Photo-Fenton reactions.*

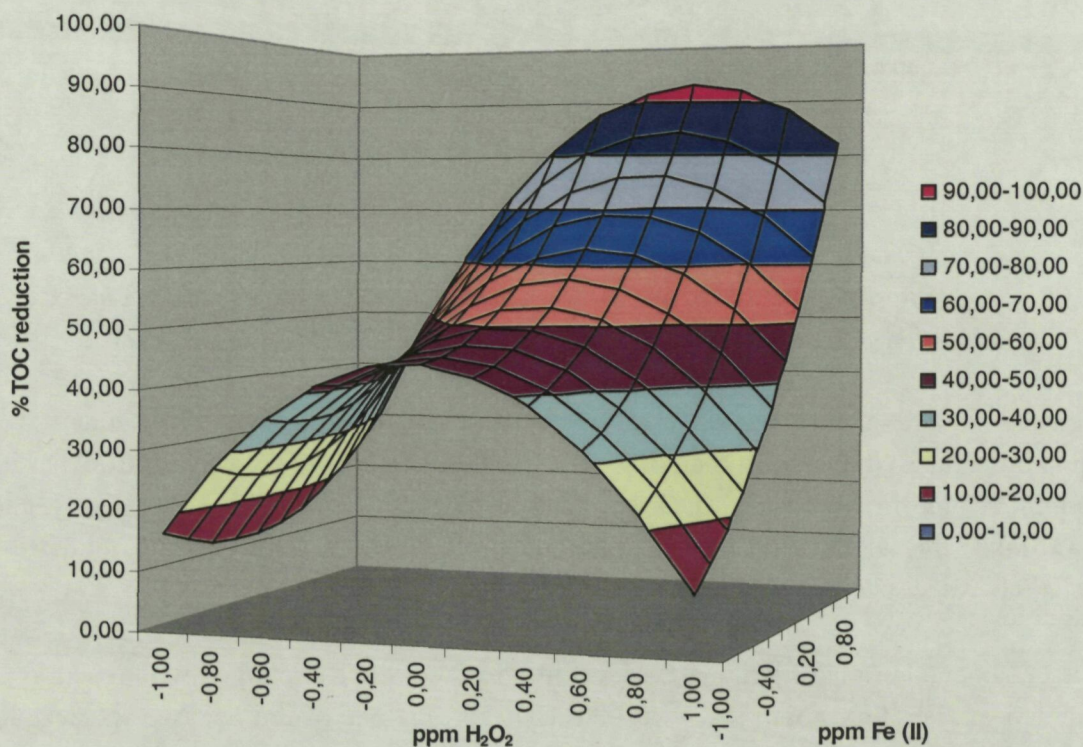
Experiment number	Codified values			Variable levels			TOC
	Temp. (°C)	[Fe(II)] (ppm)	[H ₂ O ₂] (ppm)	Temp. (°C)	[Fe(II)] (ppm)	[H ₂ O ₂] (ppm)	% Reduction
1	-1	-1	-1	30	50	1000	17.89
2	+1	-1	-1	70	50	1000	37.18
3	-1	+1	-1	30	450	1000	29.97
4	+1	+1	-1	70	450	1000	27.88
5	-1	-1	+1	30	50	10000	9.92
6	+1	-1	+1	70	50	10000	37.43
7	-1	+1	+1	30	450	10000	82.81
8	+1	+1	+1	70	450	10000	84.23
9	-1.68	0	0	16.4	250	5500	15.56
10	0	0	0	50	250	5500	83.39
11	0	0	0	50	250	5500	81.56
12	0	0	0	50	250	5500	82.54
13	-0.25	-0.625	-0.666	45	125	2500	54.73
14	0.5	-0.25	-0.333	60	200	4000	73.80

Equation 8 was obtained for the TOC removal, where Y is the response factor and X₁, X₂ and X₃ represent the variable Temperature, [Fe(II)] and [H₂O₂], respectively. Values in parenthesis describe the relative error associated to each coefficient. In those cases where the error was larger than the coefficient, it was eliminated and the variable was not expressed in the polynomial model. The explained variance for a 95% confidence level obtained by the F-test is 99.85.

$$Y (\text{TOC removal, \%}) = 82.666 (\pm 1.153) + 6.0678 X_1 (\pm 0.68) + 15.40 X_2 (\pm 0.7067) - 12.7639 X_3 (\pm 0.7073) - 20.0201 X_1^2 (\pm 0.9093) - 6.0129 X_1 X_2 (\pm 0.7073) + 1.372 X_1 X_3 (\pm 0.7066) + 14.5265 X_2 X_3 (\pm 0.70696) \quad (8)$$

From the polynomial equation it can be concluded that TOC removal is quite high during the 15 minute reaction time. For a favorable TOC reduction, the main direct effects are due to the $[\text{Fe}(\text{II})]$ and $[\text{H}_2\text{O}_2]$, but temperature also plays a significant role. An outstanding positive effect in the interaction between the variables $[\text{Fe}(\text{II})]$ and $[\text{H}_2\text{O}_2]$, (X_2X_3) is also observed. The associated effects between temperature and the Fenton reagent species are also important, especially the interaction between temperature and Fe (II) concentration (X_1X_2), which has a negative effect.

The polynomial equation allowed a three-dimensional representation of the phenomena when one of the studied parameters is fixed. The FATORIAL software [48] was used to build the response surfaces assuming that the non-fixed parameters are represented in the abscissa in coded values while the removal percentage of TOC after 15 minutes of reaction is shown in the ordinate.

a

b

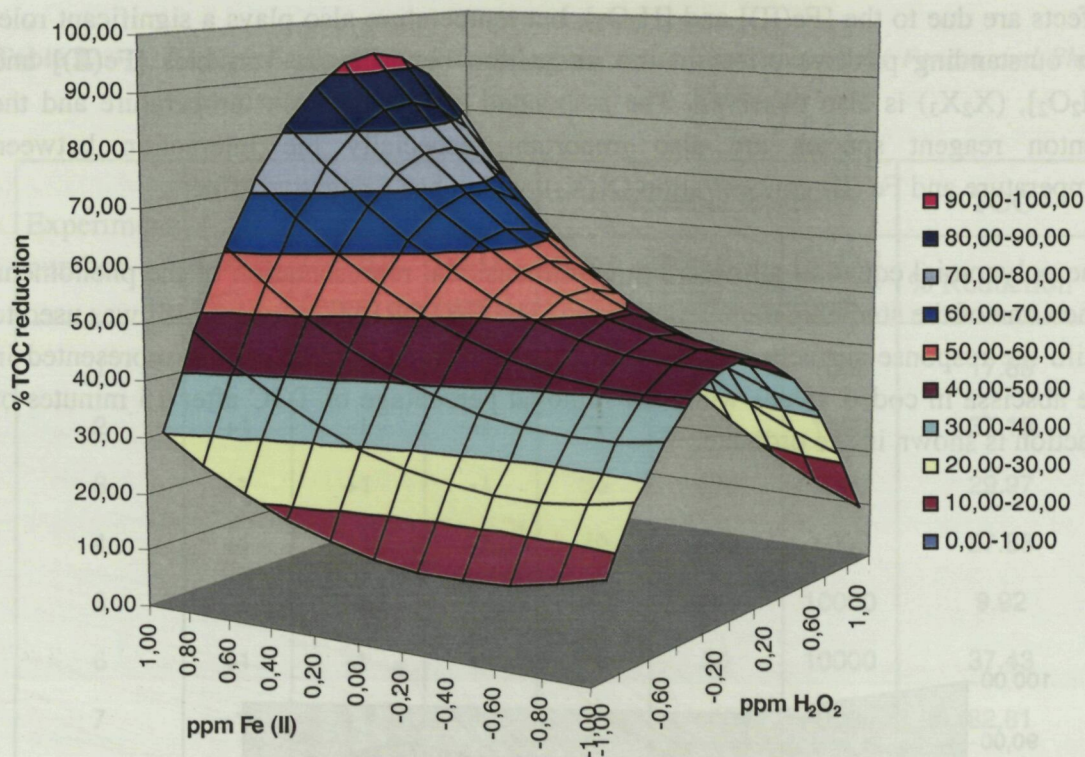


Figure 1. Three-dimensional representation of the response surface for the percentage of TOC removal after 15 minutes of reaction. Fe (II) and H_2O_2 loads are represented in coded values in the abscissa while the removal percentage is shown in the ordinate. Temperature is fixed at 30°C (the lowest value).

Figure 1, a and b, are two different views of the response surface generated with equation 8, and they show that, for all iron loads, the H_2O_2 concentration has an optimum value in which the TOC degradation reaches a maximum value. For higher H_2O_2 loads the degradation of the contaminant load decays. The effect is more clear when the iron concentration is lowest, as can be seen in figure 2.

The detrimental effect of large H_2O_2 concentrations could be explained with reaction (7) that shows that H_2O_2 could react with the OH radicals, one of the reactive species, and in this way reduce the quantity of these highly oxidative radicals present in the system. A direct consequence of the decrease of OH radicals, is the inhibition of TOC degradation.

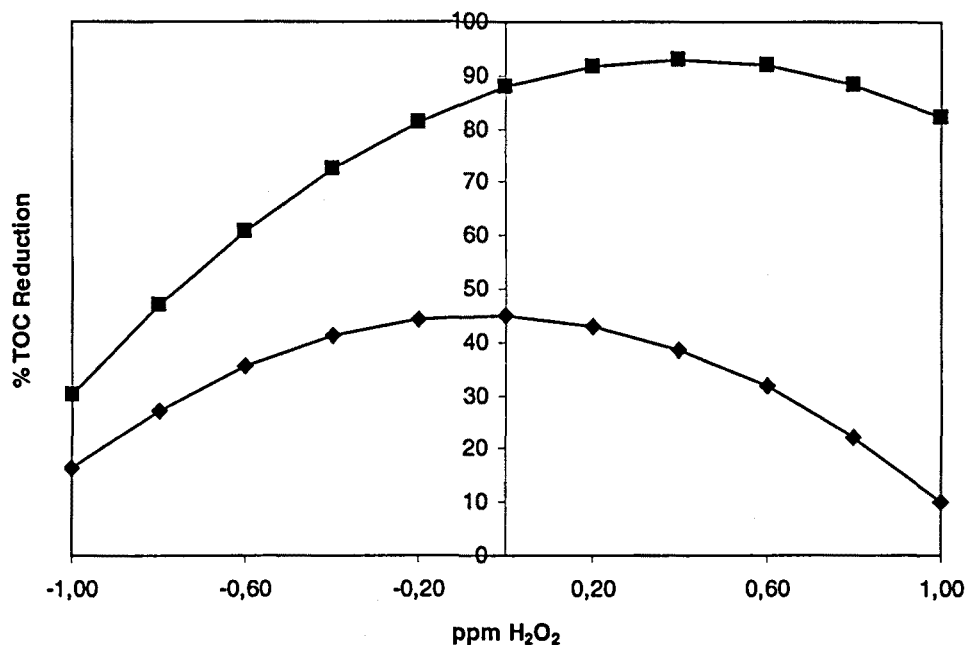


Figure 2. Percentage of TOC reduction vs. H_2O_2 concentration, for the highest iron load (■); and the lowest iron load (◆). Temperature is fixed at $30^\circ C$ (the lowest value).

Table 3 gives data of different ratios of Fenton reagent and percentages of TOC reduction for different Fe(II) initial concentration.

Table 3. Optimal ratios of Fenton reagent for different Fe(II) initial concentrations. Temperature is fixed at $30^\circ C$ (the lowest value).

Fe (II) (ppm)	Ratio H_2O_2 : Fe(II) : TOC (ppm)	% TOC reduction
50	100 : 1 : 10	45
250	25 : 1 : 2	58
450	16 : 1 : 1	93

Higher initial iron load lowers the detrimental effect of equation (7) due to a smaller excess of H_2O_2 as clearly shown in figure 2. By changing the Fenton reagent ratio from 200:1:10 to 16:1:1 while holding other experimental conditions constant, it is possible to increase the TOC reduction from 10% to 93% after 15 minutes of treatment at $30^\circ C$ and under solar light irradiation.

Similar behavior is observed when the temperature is fixed at any other value inside the studied interval. However, this tendency is less pronounced for higher temperatures.

The detrimental effect of the competitive reaction, which appear when the reagent ratio is not appropriate, is partly compensated with the positive action coming from the increasing of temperature, as will be explained below. From table 3 it is also noticeable that the initial ratio H_2O_2 : TOC must be at least 10:1 for adequate TOC removal. Consequently, when H_2O_2 concentration is fixed at lowest values, 1000 ppm (-1 codified value), the ratio H_2O_2 : TOC is lower than 2:1 and as shown in figure 1 b the TOC decay is just between 10 and 30 %.

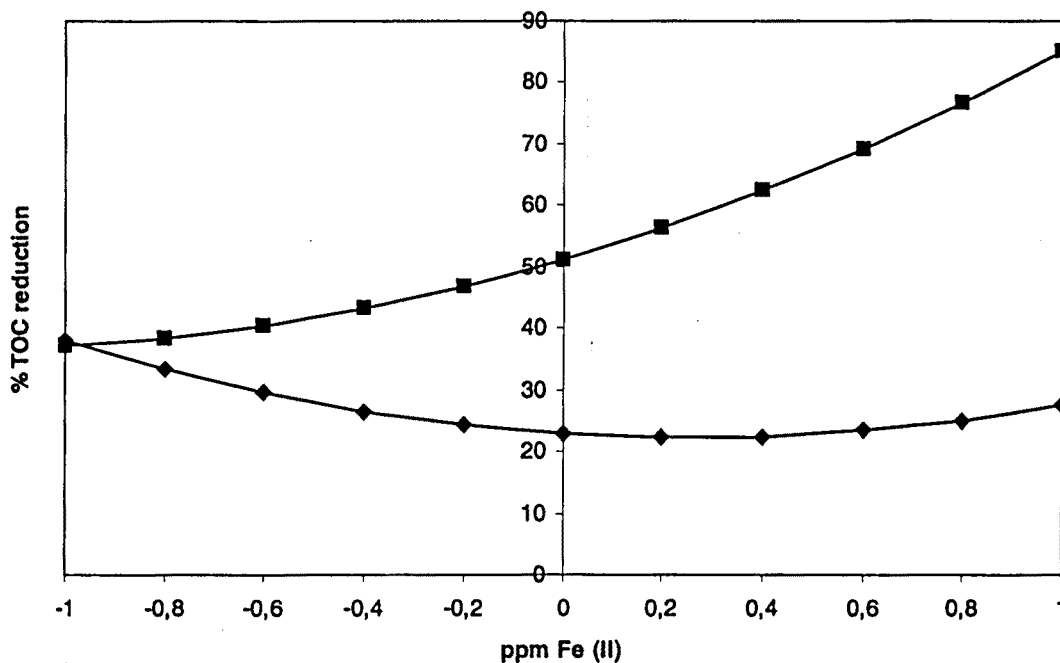


Figure 3. Percentage of TOC reduction vs. Fe (II) concentration, for the highest H_2O_2 load (■); and the lowest H_2O_2 load (◆). Temperature is fixed at 70°C (the highest value).

Figure 3 shows the evolution of the percentage of TOC reduction for different iron loads when the H_2O_2 concentration is fixed at two different values and temperature is 70°C . It is possible to distinguish two behaviors depending on the initial H_2O_2 concentration. On one hand, with the lowest H_2O_2 load and the lowest iron load the ratio H_2O_2 : Fe(II) : TOC is 20:1:10, and table 3 shows that the optimal ratio for this iron load is 100:1:10, thus these experimental conditions clearly are far from optimal. A low H_2O_2 content may cause the iron to be consumed in the competitive reaction (6). Thus, although Fenton reaction would proceed faster with a larger Fe(II) content the OH^\bullet radical can be scavenged by the Fe(II) itself (the Fe(II) that has been regenerated by photo-Fenton or Fenton like reactions), resulting in a lower TOC reduction. Therefore, the greater the initial iron load in the effluent, for these specific experimental conditions, the worse results could be expected. As can be observed in figure 3, this tendency reaches a

minimum value of TOC reduction when the reagents ratio is 6:1:3. After this point, the increase of iron load has the opposite effect: TOC decay increases as the iron load is increased. This behavior may be due to the fact that the quantity of iron is so high that it no longer acts as a catalyst. Its role in the system may rather change to that of reagent. This means the consumption of H_2O_2 takes place in the fast Fenton reaction (1) generating a large OH^\bullet concentration just when the Fe(II) concentration is low. The radicals are used for the organic matter attack and the TOC reduction. When Fe(II) is repositioned by photo-Fenton or Fenton-like reactions (slower reactions) nor OH^\bullet , neither H_2O_2 are available for Fe(II) consumption.

The system behavior for long reaction times in conditions of minimum H_2O_2 concentration and maximum iron load, as shown in figure 4, are in agreement with the above discussion: after a fast TOC decay due to the high iron content TOC reduction is stopped because the H_2O_2 concentration is exhausted.

However, when the experiments were carried out with the highest H_2O_2 concentration, the role of Fe(II) was monotonously beneficial: the higher the Fe(II) content the larger the amount of TOC reduction (see figure 3).

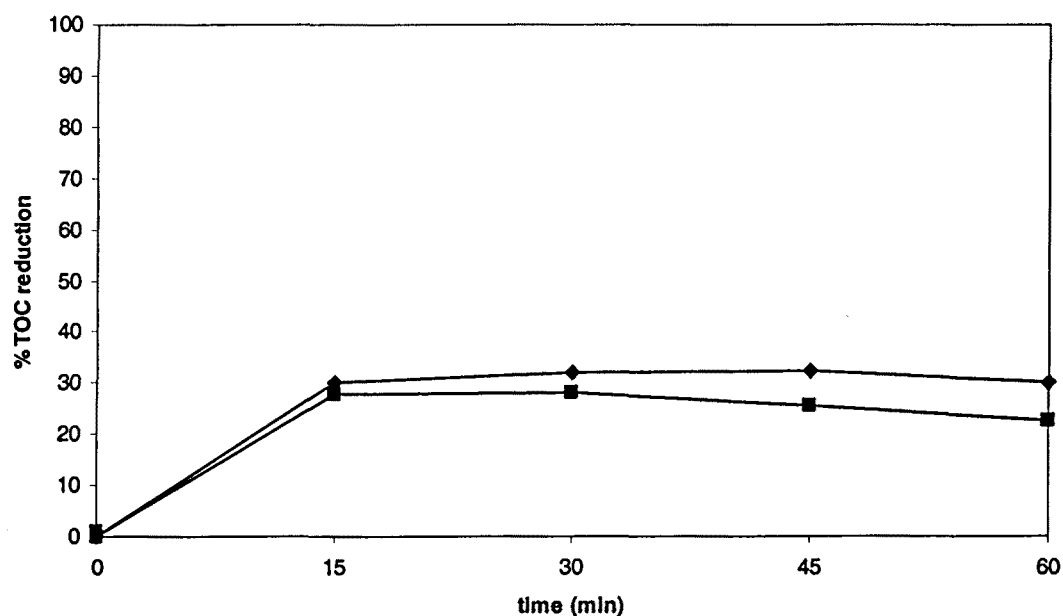


Figure 4. *Percentage of TOC reduction vs. time for the highest Fe (II) concentration and the lowest H_2O_2 load, at the lowest (30°C) (◆), and highest (70°C) (■) temperature.*

The effect of temperature can be seen in figures 5 and 6. The best TOC decrease is obtained when this parameter is settled near the central value, 50°C (central point, 0 codified value), especially for non-optimal Fenton reagent ratios.

Experiments carried out at central value concentration of hydrogen peroxide, 5500 ppm, are represented in figure 5. From this response surface, it is clearly visible that an increase of 35% in the TOC decay could take place at the lowest level of iron load by simply working in the right temperature interval. For the same Fenton reagent ratio (110 : 1 : 10) TOC reduction is 45 % when the reaction took place at 30°C temperature, and reach 80% temperature is inside the interval 45-60°C.

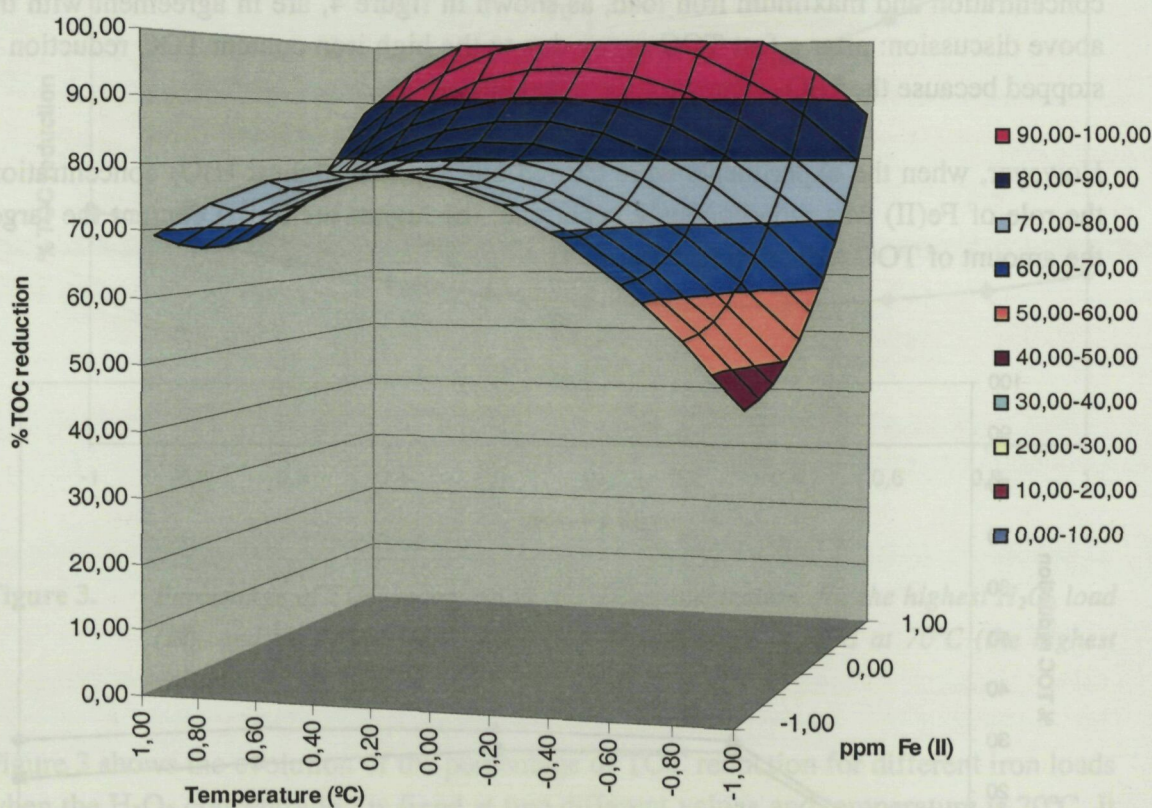


Figure 5. Three-dimensional representation of the response surface for the percentage of TOC removal after 15 minutes of reaction. Temperature and Fe (II) load are represented in the abscissa in coded values while the removal percentage is shown in the ordinate. $[H_2O_2] = 5500$ ppm (central value).

Similar behavior can be seen in figure 6, where the fixed parameter is $[Fe(II)] = 50$ ppm. Again, in this case it is advisable to use the right temperature interval, especially when the concentration of hydrogen peroxide is in its lowest value. At 30°C temperature, the percentage of TOC reduction is around 15 %, and for temperatures

inside the interval 45-65°C TOC decay is between 40 and 50 %. It is important to remark that the 35 % increase in the contaminant load degradation has been carried out in just 15 minutes of treatment.

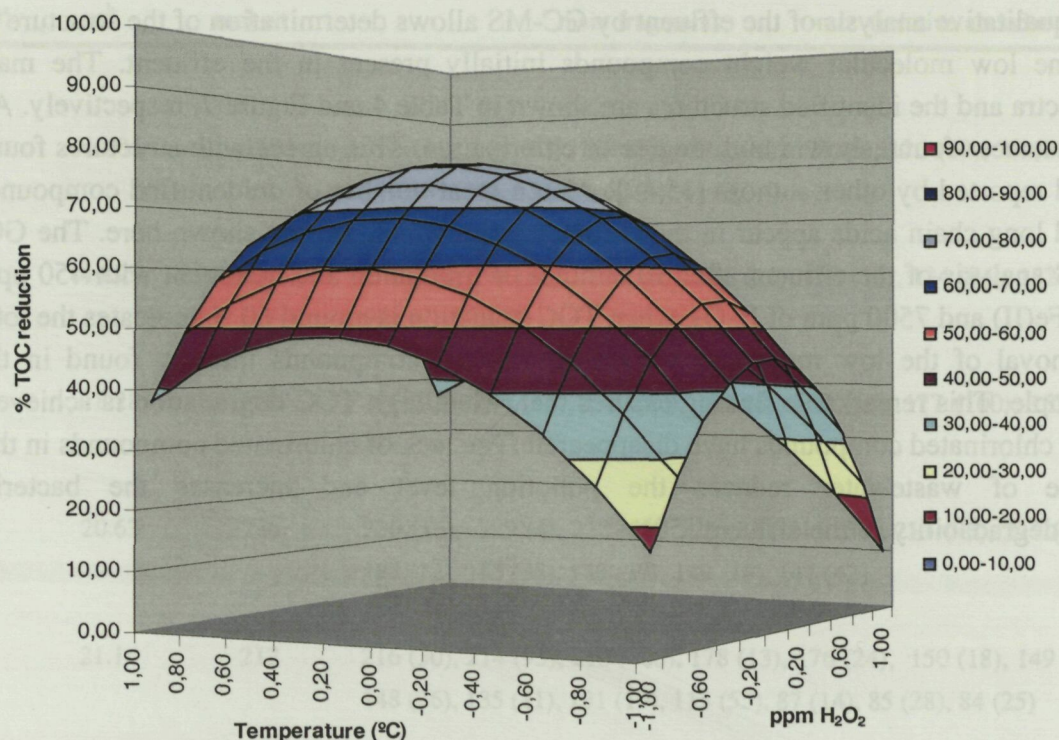


Figure 6. Three-dimensional representation of the response surface for the percentage of TOC removal after 15 minutes of reaction. temperature and H_2O_2 load are represented in the abscissa in coded values while the removal percentage is shown in the ordinate. $[Fe(II)] = 50$ ppm (the lowest studied value)

Working under adequate temperature conditions could reduce the requirements of reagents needed to reach a certain level of TOC reduction, thus decreasing the cost of the treatment. This is specially interesting when the wastewaters treated have a high temperature due to the industrial process itself, a fact that reduces the heating costs. Additionally, the use of large quantities of Fe in solution has a negative effect from the applied point of view, because it imply an additional operation for Fe removal. Thus, temperature control is an alternative way to improve the practical treatment yield.

The response surfaces clearly show that there is more than one set of experimental conditions that favor total mineralization of the organic contaminant load of the effluent. The choice of adequate experimental conditions will mainly depend on the characteristic of the effluents to be treated. In the case of a high temperature wastewater, the chosen Fenton reagent dose should be the one that ensures higher TOC decrease for

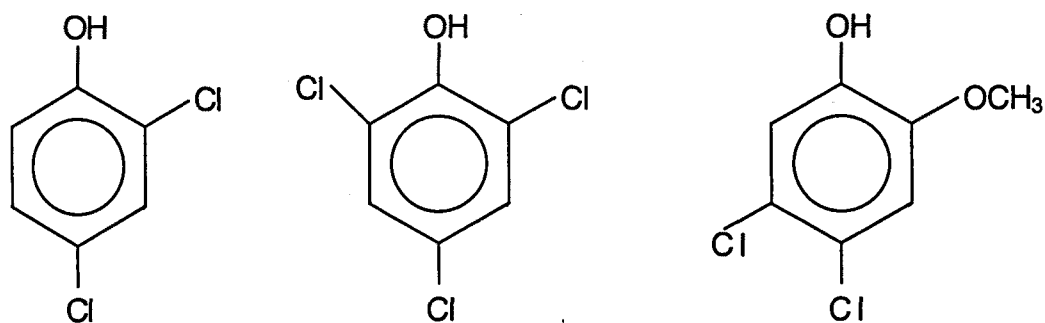
that temperature. If the wastewater should have residual iron, the process conditions should take this fact into account and the choice will have to bring the highest TOC removal for the lowest iron load.

A qualitative analysis of the effluent by GC-MS allows determination of the structure of some low molecular weight compounds initially present in the effluent. The mass spectra and the identified structures are shown in Table 4 and Figure 7, respectively. All substances found show a high degree of chlorination. This agrees with structures found and reported by other authors [15,49]. Also a great number of unidentified compounds and long chain acids appear in the chromatogram which are not shown here. The GC-MS analysis of the effluent after 30 minutes of irradiation and treatment with 450 ppm of Fe(II) and 7500 ppm of H₂O₂, when TOC reduction is around 60 % indicates the total removal of the low molecular weight chlorinated compounds initially found in the sample. This remarkable finding ensures that, when high TOC degradation is achieved, the chlorinated compounds have disappeared. The lack of chlorinated compounds in this type of wastewater reduces the pollution level and increases the bacterial biodegradability of the effluent [50].

Table 4. *Mass spectra of low molecular weight compounds identified in the bleaching Kraft mill effluent .*

# ^a	rt ^b	mol wt	main fragments	m/z (relative abundance)
1	10.04	162	166 (11), 164 (65), 163 (7), 162 (100), 127 (6), 126 (29), 99 (16), 98 (40), 81 (16), 63 (47), 62 (4), 61 (5)	
2	14.99	196	200 (27), 198 (84), 196 (100), 162 (11), 160 (15), 134 (34), 132 (51), 99 (17), 97 (42)	
3	18.28	192	196 (12), 194 (45), 192 (70), 181 (6), 179 (66), 177 (100), 153 (8), 151 (31), 149 (52)	
4	20.63	226	230 (16), 229 (4), 228 (52), 226 (54), 215 (30), 213 (95), 211 (100), 187 (12), 185 (38), 183 (39), 149 (18), 147 (42)	
5	21.16	212	216 (30), 214 (93), 212 (100), 178 (13), 176 (24), 150 (18), 149 (10), 148 (26), 135 (11), 131 (19), 113 (55), 87 (14), 85 (28), 84 (25)	
6	24.91	260	266 (5), 264 (27), 262 (60), 260 (47), 251 (9), 249 (46), 247 (98), 245 (76), 223 (4), 221 (12), 219 (27), 217 (23), 185 (7), 183 (20), 181 (21)	
7	25.20	256	260 (31), 258 (96), 256 (100), 245 (22), 243 (62), 241 (68), 215 (20), 213 (24), 202 (16), 200 (50), 198 (54), 197 (25), 195 (26)	

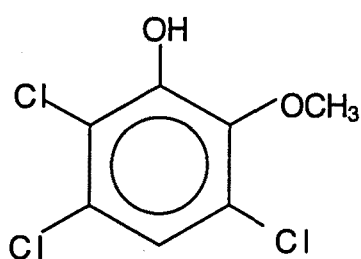
^acompound number. ^bretention time, min.



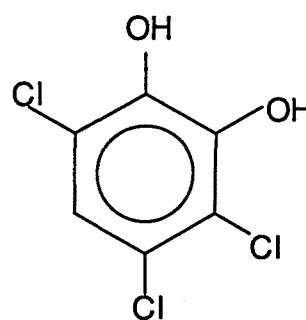
1: 2,4-dichlorophenol

2: 2,4,6-trichlorophenol

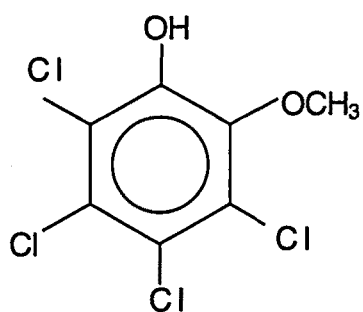
3: 4,5-dichloroguaiacol



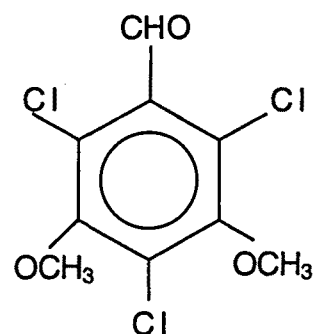
4: 3,5,6-trichloroguaiacol



5: 3,4,6-trichlorocatechol



6: tetrachloroguaiacol



7: trichlorosyringol

Figure 7. Structures of some low molecular weight compounds identified by GC-MS analysis of the chlorination bleaching step effluent before treatment.

Conclusions

The degradation of the organic content of a bleaching Kraft mill effluent has been successfully carried out by simultaneously applying Fenton reagent and solar light irradiation. Careful experimental design was valuable in determining the roles played by the different studied variables. The most important aspect that need to be considered during the treatment process is the choice of the right ratio of Fenton reagents. Non-optimal initial concentrations of Fenton reagent were found to be detrimental. This was apparently due to competitive reaction of H_2O_2 and $Fe(II)$ with the OH radical.

Temperature is a particularly significant factor for increasing TOC removal when the system runs under low reagent load or with inadequate reagent ratios. In particular, temperature turns into a key parameter when it is desirable to reduce reagents costs, or when high levels of iron are not allowed into the treated wastewaters.

Fenton, Fenton-like and Photo-Fenton reactions have been efficient in the elimination of the chlorophenolic compounds of the effluent, as shown by GC-MS analysis. The combination of Fenton reagents and solar light for the mineralization of Kraft paper mill effluents has clear advantages from an applied point of view.

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References

1. I.A. Balcioglu, I. Arslan, *Environmental Pollution* 103 (1998) 261.
2. M. Cernakova, D. Slamenova, E. Golis, L. Suty, *Folia Microbiol.* 38 (1993) 406.
3. P.F. Earl, D.W. Reeve, *Tappi J.* 73 (1990) 179.
4. R. H. Voss, J.T. Wearing, J.T. Mortimer, R.D. Kovacs, A. Wong, *Paperi ja Puu* 62 (1980) 809.
5. K.P. Kringstad, L.G. Stockman, L.M. Strönberg, *J. Wood Chem. Technol.* 4 (1984) 389.
6. M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
7. D.F. Ollis, in E. Pelizzetti, M. Schiavello, (Ed.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, Dordrecht, 1991.
8. A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735.
9. M.A. Fox, M.T. Dulay, *Chem. Rev.* 93 (1993) 341.
10. M. Pérez, F. Torrades, J.A. García Hortal, X. Domènech, J. Peral, *J. Photochem. Photobiol. A-Chem.* 109 (1997) 281.
11. A. Mills, S. Le Hunte, *J. Photochem. Photobiol. A-Chem.* 108 (1997) 1.
12. J. Reyes, M. Dezotti, H.D. Mansilla, J. Villaseñor, E. Esposito, N. Durán, *N. Appl. Catal. B-Environ.* 15 (1998) 211.
13. M.C. Yeber, J. Rodríguez, J. Freer, N. Durán, H.D. Mansilla, *Chemosphere* 41 (2000) 1193.
14. F. Torrades, J. Peral, M. Pérez, X. Domènech, J.A. García Hortal, M.C. Riva, *Tappi J.* 84 (2001) 63.
15. M. Pérez, F. Torrades, J. Peral, C. Lizama, C. Bravo, S. Casas, J. Freer, H.D. Mansilla *Appl. Catal. B-Environm* 33/2 (2001) 89.
16. M.C. Yeber, J. Rodríguez, J. Baeza, J. Freer, C. Zaror, N. Durán, H.D. Mansilla, *Wat. Sci. Technol.* 40 (1999) 337.
17. H.D. Mansilla, M.C. Yeber, J. Freer, J. Rodríguez, J. Baeza, *Wat. Sci. Tech.* 35 (1997) 273.
18. M.C. Yeber, J. Rodríguez, J. Freer, J. Baeza, N. Durán, H.D. Mansilla, *Chemosphere* 39 (1999) 1679.
19. L. Sánchez, J. Peral, X. Domènech, *App. Catal. B- Environ.* 19 (1998) 59.
20. K. Tanaka, K. Abe, T. Hisanaga, *J. Photochem. Photobiol. A-Chem.* 101 (1996) 85.
21. T.S. Muller, Z. Sun, G. Kumar, K. Itoh, M. Murabayashi, *Chemosphere* 36 (1998) 2043.
22. M. Klare, G. Waldner, R. Bauer, H. Jacobs, J.A.C. Broekaert, *Chemosphere* 38 (1999) 2013.
23. S. Hay, T.N. Obee, *J. Adv. Oxd. Technol.* 4 (1999) 209.
24. K. Krapfenbauer, N. Getoff, *Radiat. Phys. Chem.* 55 (1999) 385.
25. L. Rivas, I.R. Bellobono, F. Ascari, *Chemosphere* 37 (1998) 1033.
26. D.A. Gratson, M.R. Nimlos, E.J. Wolfrum, *Proc. Annual Meeting Air Waste Manage. Assoc. Publ.*, 88 (1995) 11.

27. H. Mao, D.W. Smith, *Ozone Sci. Eng.* 17 (1995) 205.
28. Peyton, G.R., in *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, Lewis Publishers, Chelsea, 1990, p. 313.
29. E. Chamarro, A. Marco, S. Esplugas, *Water Research* 35 (2001) 1995.
30. G. Ruppert, R. Bauer, G. Heisler, *J. Photochem. Photobiol. A: Chem.* 73 (1993) 75.
31. M. Pérez, F. Torrades, J.A. García Hortal, X. Domènech, J. Peral, Submitted for publication to *Appl. Catal. B-Environ.*
32. J. Kiwi, C. Pulgarin, P. Peringer, *Appl. Catal. B-Environ.* 3 (1994) 335.
33. W.Z. Tang, C.P. Huang, *Environ. Technol.* 17 (1996) 1371.
34. A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, *J. Advan. Oxid. Technol.* 1 (1996) 1.
35. R. Bauer, H. Fallmann, *Res.Chem.Intermed.* 23 (1997) 341.
36. J.J. Pignatello, *Environ. Sci. Technol.* 26 (1992) 944.
37. Y. Sun, J.J. Pignatello, *Environ.Sci. Technol.* 27 (1993) 304.
38. J.J. Pignatello, D. Liu, P. Huston, *Environ. Sci. Technol.* 33 (1999) 1832.
39. S.H. Bossmann, E. Oliveros, S. Göb, S. Siegwart, E.P. Dahlen, L. Payawan, M. Straub, M. Wörner, A.M. Braun, *J. Phys. Chem.* 102 (1998) 5542.
40. J.C. Lescot, H. Jappinen, *Appita J.* 47 (1994) 330.
41. J. Rodríguez, S. Fuentes, J. Freer, H.D. Mansilla, A. Ferráz, J. Baeza, *Environ. Technol.* 19 (1998) 75.
42. E. Oliveros, O. Legrini, M. Hohl, T. Müller, A.M. Braun, *Wat. Sci. Technol.* 35 (1997) 223.
43. Canadian Pulp and Paper Association Standard Method H.5 – Color of Pulp Mill Effluents (Approved method, December 1991; Revised, August 1993)
44. Standard Methods for the examination of water and wastewater nº 5220 C, 20th Edition, (1999)
45. H-J. Benkelberg, P. Warneck, *J. Phys. Chem.* 99 (1995) 5214.
46. K.A. Hislop, J.R. Bolton, *Environ. Sci. Technol.* 33 (1999) 3119.
47. M. Barbeni, C. Minero, E. Pelizzetti, E. Borgarello, N. Serpone, *Chemosphere* 16 (1987) 2225
48. B. de Barros Neto. I.S. Scarminio, R.E. Bruns, in Unicamp (Ed.), *Planejamento e Otimização de Experimentos*, Brazil, 1996.
49. T.Y. Tsai, J.J. Renard, R.B. Phillips, *Tappi J.* 77 (1994) 149.
50. M.C. Yeber, J. Freer, M. Martínez, H.D. Mansilla, *Chemosphere* 41 (2000) 1257.

Paper 7

Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent

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Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent

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Abstract

TiO₂-photocatalytic degradation of a cellulose ECF effluent was evaluated using multivariate experimental design. The effluent was characterised by general parameters such as AOX, TOC, COD, colour, total phenols, acute toxicity and by the analysis of chlorinated low molecular weight compounds using CG/MS. The pH, catalyst amount and hydrogen peroxide were simultaneously varied using multivariate analysis to establish the weight of each variable in the COD and AOX removal after 180 min of reaction. The pH has a large effect in the AOX degradation at values below 5 and over 10, while COD removal is improved at low pH. The presence of hydrogen peroxide in the photocatalytic reaction has a small effect in degrading the AOX and COD. The optimal concentration of TiO₂ was found to be around 1 g l⁻¹. In addition, the reaction was monitored for longer periods of irradiation by carrying out TOC, COD, AOX, acute toxicity and spectrophotometric analysis, concluding that the organic matter contained in the effluent was significantly degraded. After 30 min of reaction more than 60% of the toxicity was removed and after 420 min of reaction none of the initial chlorinated low molecular weight compounds were detected, suggesting an extensive mineralisation which was corroborated by 95 and 50% AOX and TOC removals, respectively. Colour and total phenols were also removed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cellulose bleaching effluent; Chlorinated phenols; Experimental design; Multivariate analysis; Photocatalysis; Effluent toxicity

1. Introduction

Chlorinated phenols and polyphenolic compounds are important components of effluents arising from the bleaching of papermaking pulps with either molecular chlorine or chlorine dioxide [1]. These sub-

stances as well as unchlorinated phenols, have been the sources of environmental concern due to their toxicity, bio-accumulation and carcinogenic potential [2,3], which increase with an increase in the number of chlorine atoms per molecule [4,5].

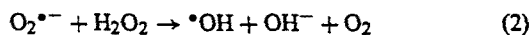
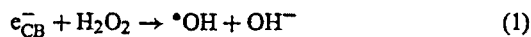
When molecular chlorine is replaced by chlorine dioxide in the ECF bleaching process, the amount of chlorinated phenols formed in the chlorination and extraction stage effluents significantly decreases [3]. However, little amounts of chlorinated phenols remain

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in solution even in a chlorine dioxide ECF bleaching sequence. Because, the toxicity of chlorophenols and the risk to the aquatic environment we have focused our attention on such compounds even though they do not constitute the major fraction of the compounds contained in the effluent.

Conventional treatments of cellulose mill effluents involve a biological step such as aerated lagoons or activated sludge. However, when dissolved compounds are toxic or recalcitrant, the biological treatments can be inhibited or simply the microbiological flora destroyed. Several attempts have been done in order to reduce the organic charge in cellulose mill effluents before the biological step. The emerging advanced oxidation processes, such as ozone [6], O₃ combined with UV light [7], homogeneous and heterogeneous AOPs [8] and combined photochemical–biological systems [9] have been reported in the treatment of cellulose mill effluents. More recently, photocatalytic reactions have been used to degrade pulp mill effluents seeing the removal of the dissolved organic matter improving the biodegradability and reducing the acute toxicity [10]. Pérez et al. [11] demonstrates that TiO₂ based photocatalysis was very efficient in the removal of colour and TOC of an ECF effluent, a process that follows a zero order kinetics. On the other hand, Yeber et al. [12] showed that total phenols and colour can be almost completely eliminated after 2 h of irradiation in concomitance with the degradation of the high molecular weight polyphenols, when glass supported TiO₂ or ZnO were used.

Several publications have considered the use of hydrogen peroxide in the photocatalytic system UV/TiO₂ in order to produce additional hydroxyl radicals. Two possible roles have been proposed for H₂O₂: (a) alternative electron acceptor to oxygen at the conduction band (Eq. (1)) or (b) electron acceptor of the superoxide anion (Eq. (2)).



Recently, Bacsa and Kiwi [13] reported the enhancement of the *p*-coumaric acid degradation by addition of hydrogen peroxide (2 mM) to the TiO₂ photocatalytic system. On the other hand, Brillas et al. [14] reported the acceleration of the aniline mineralisation by TiO₂ photocatalysis after addition of 1 mM

H₂O₂. Cornish et al. [15] observed a significant enhancement of the toxin microcystin-LR mineralisation and a considerable acute toxicity removal by the addition of H₂O₂ to the TiO₂ photoassisted oxidation.

Multivariate analysis has become an important tool to get valuable and statistically significant model of a phenomenon by performing a minimum set of well chosen experiments. With a determined number of assays, it can obtain information regarding with the importance of each variable and the interaction effects between them. Also, it is possible to calculate the optimal conditions to get the most desirable response. Applications of this statistical methodology have been reported for pulp mill effluent treatment with ozone [16] and in the Fenton reaction of industrial wastewater's containing aromatic amines [17].

The aim of this report is to study a cellulose effluent photodegradation in order to reduce the amount of chlorinated compounds, colour, acute toxicity and organic load. The experimental design methodology was used to evaluate the importance of catalyst mass, the pH and the presence of hydrogen peroxide in the AOX and COD removal. Also, COD, TOC, toxicity and spectrophotometric analysis of the effluent in the course of the reaction were carried out at longer periods of reaction.

2. Experimental

2.1. Effluent and reagents

The first alkaline extraction effluent obtained from a Chilean pulp mill, after the bleaching sequence D₀E₀P₁D₁D₂ (ECF) of *Pinus radiata* kraft pulp, was stored at –4°C and used as received. Hydrogen peroxide (30%) was obtained from Riedel-de-Haën and titanium dioxide was Degussa P25. All the other reagents were purchased from Merck and used without further purification.

2.2. Photocatalytic reaction

Photolysis assays were carried out in a 1.1 l cylindrical photochemical reactor, with suspended TiO₂ and refrigerated with tap water to keep the temperature at 25°C. The configuration of the reactor has been previously described [12]. A Philips 125 W

high-pressure mercury lamp ($\lambda > 254$ nm) placed in a quartz tube immersed in the treated solution was used as irradiation source. The reaction was initiated after 30 min of magnetic stirring of the suspension in the dark. Total UV incident radiation flux was determined by potassium ferrioxalate actinometry (5.9×10^{-5} Einstein $l^{-1} s^{-1}$) [18]. The real output of the lamp in the 250–300 nm region was determined by actinometry using a Pyrex filter, and it was 37% of the total emission.

2.3. Analytical methods

Chemical oxygen demand (COD) was determined by standardised methodology (EPA 00340). Adsorbable organic halogen (AOX) was measured by the recommended procedure (AOXDIN/38409-H14) in an EUROGLAS ECS-1000 AOX analyser. UV–VIS spectra and colorimetric determinations were done in a Shimadzu 1603A spectrophotometer. Total organic carbon (TOC) analyses were carried out in a TOC-5000 Shimadzu analyser. Total phenol determinations were done using the standard procedure [19] and represent the sum of simple phenols and high molecular weight phenolic compounds (lignin and tannins). Colour was determined at 465 nm and referenced to a Pt–Co standard solution (EPA 00080).

For the analysis of low molecular weight compounds dissolved in the effluent a HP 5890 series II gas chromatograph equipped with a HP 5972 mass selective detector was used. One litre of the sample was filtered in Speedisk[®] membrane (Baker) following the recommended procedure (EPA 525). Samples were concentrated to 200 μ l in dichloromethane and 1 μ l was injected in the GC. After that the same sample was diluted to 2 ml with dichloromethane and derivatised by methylation with diazometane according with the standardised procedure [20] and then 1 μ l was injected to the GC. In samples with and without derivatisation identical results were obtained. Identifications were carried out with the aid of the data base library incorporated to the MS instrument and with a database generated with own standards.

The acute toxicity test was performed by MICROTOX[®] using the *Vibrio fischeri* luminescence inhibition to assess the EC₅₀ values. The results are expressed as toxicity units (TU) which was defined as 100/EC₅₀.

3. Results and discussion

The Table 1 summarises the main features of the effluent used in this study. The magnitudes reveal high colour, COD, TOC and a large amount of organochlorine phenols as shown by AOX values and a moderate acute toxicity. The photocatalysed degradation of the cellulose bleaching effluent was carried out in order to reduce the initial parameters responsible of its environmental impact. The removal of organochlorinated compounds, colour and TOC are the main goals of this study, in an attempt to obtain effluents ready for a biological treatment.

In the present paper we have studied the effect of H₂O₂ addition to a photocatalytic system degrading the organic matter dissolved in the cellulose bleaching effluent in order to evaluate the incidence of this variable in the AOX and COD removal. The reaction was carried out both in absence of H₂O₂ and for increasing amounts of the reagent up to the maximum value of 1 mM. The weight of the variables pH and TiO₂ concentration, ranging from 5 to 10 and 0.5 to 1.5 g l⁻¹, respectively, were also evaluated. The natural pH of the effluent was 7.2 and the range of variation was chosen considering that it is not economically convenient to make great changes in this parameter. The amounts of TiO₂ used were in the range normally reported for photocatalytic degradation of pure compounds or complex effluents.

A factorial experimental design (2³) was carried out considering low and high levels for pH (5–10), TiO₂ (0.5–1.5 g l⁻¹) and H₂O₂ (0–1 mM). Table 2 contains the description of the experiments. Low and high levels and central points are denoted by (–), (+) and (0), respectively. From the values shown in Table 2 and as-

Table 1
Initial characterisation of the ECF effluent

Parameter	Value
TOC (ppm C)	487
pH	7.2
Toxicity (EC ₅₀)	36.5
COD (mg O ₂ l ⁻¹)	1400
AOX (ppm) ^a	58
Lignins and tanins (ppm) ^b	40
Colour (mg Pt l ⁻¹)	2100

^a Organic chlorine l⁻¹ (mg).

^b Phenol l⁻¹ (mg).

Table 2
Factorial design of the TiO₂ photocatalysed reaction of the ECF effluent

Experiment No.	Variable levels (codified values)			COD reduction (%)	AOX reduction (%)
	pH	[TiO ₂]	[H ₂ O ₂]		
1	5.0 (-1)	0.5 (-1)	0.0 (-1)	16	64.0
2	10.0 (+1)	0.5 (-1)	0.0 (-1)	16	70.7
3	5.0 (-1)	1.5 (+1)	0.0 (-1)	14	75.7
4	10.0 (+1)	1.5 (+1)	0.0 (-1)	14	75.8
5	5.0 (-1)	0.5 (-1)	1 × 10 ⁻³ (+1)	13	63.7
6	10.0 (+1)	0.5 (-1)	1 × 10 ⁻³ (+1)	10	69.4
7	5.0 (-1)	1.5 (+1)	1 × 10 ⁻³ (+1)	25	73.4
8	10.0 (+1)	1.5 (+1)	1 × 10 ⁻³ (+1)	20	73.3
9	3.3 (-2.82 ^{1/2})	1.0 (0)	5.0 × 10 ⁻⁴ (0)	24	70.0
10	11.7 (2.82 ^{1/2})	1.0 (0)	5.0 × 10 ⁻⁴ (0)	16	72.0
11	7.5 (0)	0.2 (-2.82 ^{1/2})	5.0 × 10 ⁻⁴ (0)	1	57.0
12	7.5 (0)	1.8 (2.82 ^{1/2})	5.0 × 10 ⁻⁴ (0)	7	63.6
13	7.5 (0)	1.0 (0)	1.3 × 10 ⁻³ (2.82 ^{1/2})	18	70.0
Central point	7.5 (0)	1.0 (0)	5.0 × 10 ⁻⁴ (0)	20	69.0
	7.5 (0)	1.0 (0)	5.0 × 10 ⁻⁴ (0)	21	70.7

suming a second order polynomial model, at least 13 experiments must be carried out to solve the matrix (including the interaction effects between variables) and the error evaluation.

The matrix was resolved using the software FATORIAL [21] and considering the percentage of COD and AOX removal after 3 h of irradiation as the response factors. The coefficients of the quadratic model in the polynomial expression were calculated by multiple regression analysis, and represent the weight of each variable, the quadratic effect and the first-order interaction between the coded variables. Eqs. (3) and (4) were obtained for the AOX and COD removal, where Y is the response factor and X_1 , X_2 and X_3 represent the variable pH, [TiO₂] y [H₂O₂], respectively. Values in parenthesis describe the relative error associated to each coefficient. In the case that error was larger than the coefficient, it was eliminated and the variable was not expressed in the polynomial model. Also, the explained variance for 95% confidence level is shown.

$Y(\text{AOX removal, \%})$

$$\begin{aligned}
 &= 69.63(\pm 1.42) + 1.23X_1(\pm 0.67) \\
 &+ 3.23X_2(\pm 0.67) - 1.33X_3(\pm 0.82) \\
 &+ 1.50X_1^2(\pm 0.75) - 3.83X_2^2(\pm 0.75) \\
 &+ 2.56X_3^2(\pm 0.91) - 1.55X_1X_2(\pm 0.87),
 \end{aligned}$$

$$\begin{aligned}
 &\% \text{ of explained variance} \\
 &= 94.2 \text{ (95\% confidence)} \quad (3)
 \end{aligned}$$

$Y(\text{COD removal, \%})$

$$\begin{aligned}
 &= 20.26(\pm 1.61) - 1.69X_1(\pm 0.75) \\
 &+ 1.87X_2(\pm 0.75) - 6.31X_2^2(\pm 0.85) \\
 &+ 3.25X_2X_3(\pm 0.99), \\
 &\% \text{ of explained variance} \\
 &= 94.8 \text{ (95\% confidence)} \quad (4)
 \end{aligned}$$

From polynomial equations it can be concluded that the AOX removal is higher than COD in the time considered as response factor (3 h). For a favourable AOX reduction the main direct effects are due to the TiO₂ amount followed by the pH. On contrary, the increase of hydrogen peroxide concentration is detrimental to get the same objective. The associated effects between variables are neglected except in the interaction between pH and TiO₂ amount (X_1X_2), which shows an antagonistic effect.

In the COD removal, the most important positive effect is also due to TiO₂ amount, pH shows a negative effect and H₂O₂ do not play a significant role. An important synergistic effect in the interaction between the variables TiO₂ amount and H₂O₂ concen-

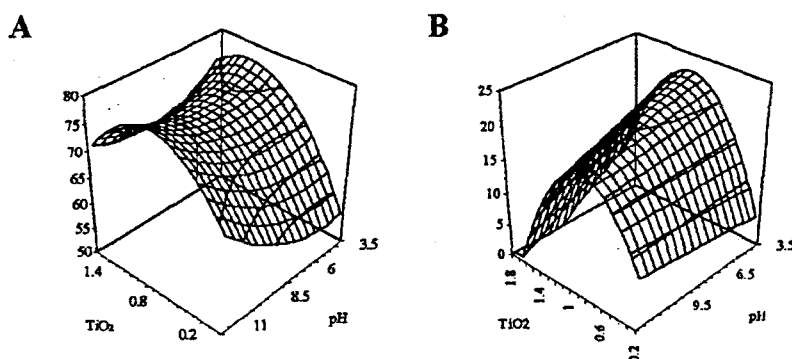


Fig. 1. Three-dimensional representation of the response surface for the percent of AOX (A) and COD removal (B), after 3 h of photocatalysis. TiO_2 load and pH are represented in the abscissa, while in the ordinate the removal percent of each parameter is shown.

tration (X_2X_3) was observed. In spite of the evidence presented in the literature regarding with the mineralisation enhancement of pure substances with the H_2O_2 addition, in the case of a complex and coloured solution, as our effluent, this effect was not observed. Recently, Dionysiou et al. [22] showed that the addition of H_2O_2 to 4-chlorobenzoic acid solution results in an increase of the photocatalytic reaction rates only at concentrations below 7.5 mM. The optimal pH values were found to be out of the pH range considered in the study. This fact can be clearly observed in Fig. 1(A and B), where a three-dimensional representation of the phenomena is shown. Response surfaces were built assuming that the concentration of H_2O_2 was zero, taken in account its low concentration and moderate importance in the removal of AOX and COD.

In the AOX response surface, it can be seen that the optimal pH values are placed below 5 and beyond 10. A similar trend was observed in a previous report for TiO_2 photocatalysis of aniline [23]. On the other hand, the COD removal is improved at low pH. The optimal amount of TiO_2 was around 1 g l^{-1} for both AOX and COD removal. This value agrees with the reported ones obtained by other procedures. Once the optimal amount of TiO_2 was determined, the AOX, COD and TOC degradation profiles were followed for larger periods of time. A minimal concentration of H_2O_2 ($1 \times 10^{-4} \text{ M}$) was used for kinetic experiments considering the interaction effect X_2X_3 in the COD removal and the quadratic effect (X_2^2) in the AOX removal. Taken in consideration that the optimal pH

found was out of the studied range, and due to the fact that this parameter is more difficult to control in an industrial operation, the kinetics were carried out at natural pH (7.2).

In previous communications [8–12,24], we have reported the photocatalytic degradation of different pulp and paper mill effluents using TiO_2 and ZnO as photocatalysts with promissory results. The decrease of acute toxicity, which is concomitant with the AOX removal and the increase of biodegradability, has been the most remarkable results. The photocatalyst have been tested either on aqueous suspension or immobilised on glass Raschig rings.

The Fig. 2a shows the profile of AOX removal, where a significant decrease is observed. A 50% reduction was obtained after 90 min of reaction reaching an almost complete mineralisation of organic chlorine after 7 h of photoreaction. A qualitative analysis of the effluent by GC/MS allowed us to determine the structure of some low molecular weight compounds present in the initial effluent. The mass spectra and the identified structures are shown in Table 3 and Fig. 3, respectively. All the substances found show high chlorination degree, which agree with the initially high AOX value. Similar structures were found and reported by other authors [25]. Also in the chromatogram appears a great number of unidentified compounds and long chain acids, which are not shown here. The GC/MS analysis of the effluent after 7 h of irradiation indicates the total removal of the low molecular weight chlorinated compounds initially found in the sample. This

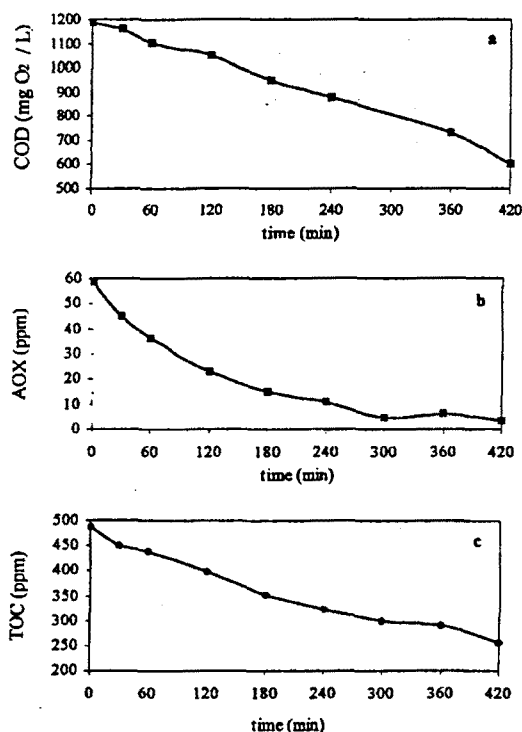


Fig. 2. Kinetic of the removal under optimised conditions for TiO_2 amount (1.04 g l^{-1}), pH 7.2 and $1 \times 10^{-4} \text{ M H}_2\text{O}_2$ for: (a) AOX; (b) COD and (c) TOC.

finding agree with recent published results where, after few hours of irradiation, a significant degradation of 6-chlorovanillin, used as a model compound for chlorinated effluents, was reported, increasing their bacterial biodegradability [26].

The progress of the COD during the reaction was also determined and results are shown in the Fig. 2b. The parameter decreases with an approximate zero order kinetics, which is expected for concentrated and complex solutions. A 50% of COD removal was obtained over 6 h of irradiation.

While, COD represents the amount of oxygen demand by organic or inorganic material dissolved in the effluent, the TOC measures the TOC and a decrease in this parameter is indicative of the organic matter mineralisation. The TOC removal progress during the photocatalysis is shown in Fig. 2c, where an approximated zero order kinetics is observed, with a similar profile to COD removal. 50% of TOC removal was reached after 7 h of irradiation meaning that the major part of COD removed corresponds to the total mineralisation of the organic matter. Partial mineralisation along with structural changes in the organic matter have been reported as being fundamental for the biodegradability increase and toxicity abatement of the cellulose mill effluents and chlorinated phenols [9,26].

Other studied parameter was the total phenols content which follows a random behaviour increasing their value during the first 2 h of photocatalysis and then reaching 60% of reduction after 7 h of irradiation (data not shown). These finding suggest that a simultaneous hydroxylation of aromatic groups with loss of chlorine atoms initially occurs, leading to the

Table 3
Mass spectra of low molecular weight compounds identified in the ECF bleaching effluent

Compound No.	Retention time (min)	mol wt.	Main fragments m/z (relative abundance)
1	12.22	196	200 (30), 198 (93), 196 (100), 162 (10), 160 (14), 134 (23), 132 (36), 99 (16), 97 (41)
2	12.76	192	196 (1), 194 (45), 192 (76), 181 (13), 179 (75), 177 (100), 153 (7), 151 (31), 149 (40)
3	13.98	192	196 (8), 194 (47), 192 (76), 181 (10), 179 (65), 177 (100), 153 (6), 151 (35), 149 (54)
4	14.97	186	188 (31), 187 (40), 186 (89), 185 (100), 173 (14), 171 (4), 145 (7), 143 (18), 117 (9), 115 (28)
5	15.18	226	230 (33), 229 (7), 228 (82), 226 (79), 215 (32), 213 (100), 211 (92), 187 (28), 185 (71), 183 (44), 149 (21), 147 (35)
6	15.33	226	230 (16), 229 (5), 228 (51), 226 (55), 215 (30), 213 (94), 211 (100), 187 (12), 185 (39), 183 (40), 149 (35), 147 (31)
7	16.80	226	230 (28), 229 (8), 228 (88), 226 (84), 215 (31), 213 (100), 211 (94), 187 (13), 185 (46), 183 (44), 149 (29), 147 (40)
8	17.72	260	266 (8), 264 (31), 262 (64), 260 (49), 251 (9), 249 (47), 247 (100), 245 (78), 223 (5), 221 (20), 219 (43), 217 (31), 185 (8), 183 (22), 181 (21)

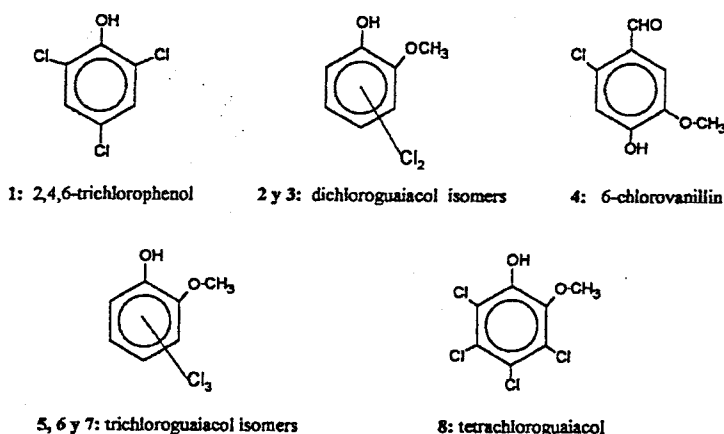


Fig. 3. Structures of some low molecular weight compounds identified by CG/MS analysis in the initial ECF bleaching effluent.

breaking of aromatic ethers in high molecular weight polyphenols, and increasing the phenolic groups content. The decrease of total phenolic groups, compared to the initial value (40 ppm), was observed after 3 h of irradiation and is explained by ring opening, generation of more oxidised molecules (hydroquinones and quinones) and, finally, partial or total mineralisation.

Spectral behaviour of treated samples is shown in the Fig. 4. The family of curves represents the UV–VIS spectra of samples treated at different periods of irradiation on 15-fold diluted samples. A gradual decrease in the absorption spectra is indicative of the rapid degradation of chromophoric groups. The formation of new chromophores was not observed in the course of the

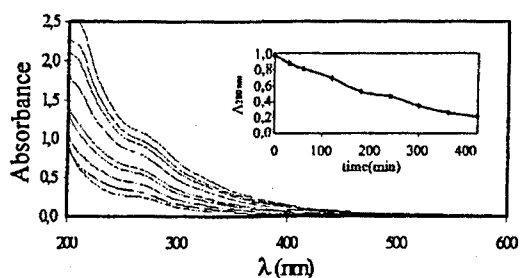


Fig. 4. Decolouration profile of the ECF effluent. In decreasing sequence the curves represent the spectra at 0, 30, 60, 120, 180, 240, 300, 360 and 420 min of irradiation under optimised conditions.

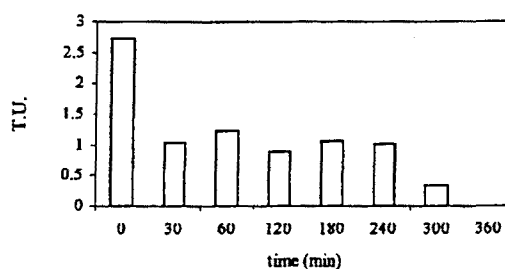


Fig. 5. Acute toxicity removal (MICROTOX) in TU defined as 100/EC₅₀.

reaction. The graphic inserted in the same figure shows that the absorbance at 280 nm rapidly decreases along with rapid colour changes of the suspensions, which were visually evident after few minutes of irradiation.

In the chemical treatment of solutions containing organochlorine compounds, the most important aimed result is their detoxification in a short period of time. In Fig. 5, the acute toxicity changes during the progress of the photocatalytic reaction are shown. A rapid and significant decrease (63%) is observed after 30 min of reaction, reaching the total removal after 360 min. It is probable that the rapid initial reduction of the acute toxicity was achieved during the first minutes of irradiation as it has been previously reported [9,26].

4. Conclusions

The experimental design has been a valuable methodology to set up the role that the variables studied in the photocatalysis of cellulose bleaching effluent plays. The most significant effect was ascribed to pH and TiO₂ load. The H₂O₂ concentration has no positive effect in the AOX removal, at least in the range studied, but it shows a first-order interaction with the catalyst amount, enhancing the COD removal. The photocatalysis has been efficient in the reduction of the most important parameters that account for the environmental impact such as AOX, TOC and total phenols. The toxicity was significantly removed from the solution during the first stages of the reaction.

Acknowledgements

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References

- [1] T.J. Smith, R.H. Wearne, A.F.A. Wallis, *Chemosphere* 28 (1994) 921.
- [2] M. Cernakova, D. Slaménova, E. Golis, L. Suty, *Folia Microbiol.* 38 (1993) 406.
- [3] P.F. Earl, D.W. Reeve, *Tappi J.* 73 (1990) 179.
- [4] R.H. Voss, J.T. Wearing, J.T. Mortimer, R.D. Kovacs, A. Wong, *Paperi Puu* 62 (1980) 809.
- [5] K.P. Kringstad, L.G. Stockman, L.M. Strönberg, *J. Wood Chem. Technol.* 4 (1984) 389.
- [6] H. Mao, D.W. Smith, *Ozone Sci. Eng.* 17 (1995) 205.
- [7] C. Prat, M. Vicente, S. Esplugas, *Ind. Eng. Chem. Res.* 29 (1990) 349.
- [8] H.D. Mansilla, M.C. Yeber, J. Freer, J. Rodríguez, J. Baeza, *Water Sci. Technol.* 35 (1997) 273.
- [9] J. Reyes, M. Dezotti, H.D. Mansilla, J. Villaseñor, E. Esposito, N. Durán, *Appl. Catal. B* 15 (1998) 211.
- [10] M.C. Yeber, J. Rodríguez, J. Baeza, J. Freer, C. Zaror, N. Durán, H.D. Mansilla, *Water Sci. Technol.* 40 (1999) 337.
- [11] M. Pérez, F. Torrades, J.A. Garcia-Hortal, X. Doménech, J. Peral, *J. Photochem. Photobiol. A: Chem.* 109 (1997) 281.
- [12] M.C. Yeber, J. Rodríguez, J. Freer, N. Durán, H.D. Mansilla, *Chemosphere* 41 (2000) 1193.
- [13] R.R. Bacsa, J. Kiwi, *Appl. Catal. B* 16 (1998) 19.
- [14] E. Brillas, E. Mur, R. Saudela, L. Sánchez, J. Peral, X. Doménech, J. Casado, *Appl. Catal. B* 16 (1998) 31.
- [15] B.J.P.A. Cornish, L.A. Lawton, P.K.J. Robertson, *Appl. Catal. B* 25 (2000) 59.
- [16] J. Rodríguez, S. Fuentes, J. Freer, H.D. Mansilla, A. Ferráz, J. Baeza, *Environ. Technol.* 19 (1998) 75.
- [17] E. Oliveros, O. Legrini, M. Hohl, T. Müller, A.M. Braun, *Water Sci. Technol.* 35 (1997) 223.
- [18] S.L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, p. 119.
- [19] APHA Standard Method for Examination of Water and Wastewater, 17th Edition, New York, Am. Publ. Health Assoc. 5550 (1989) 5.68.
- [20] Aldrich, *Technical Information Bulletin*, AL-180.
- [21] B. de Barros Neto, I.S. Scarminio, R.E. Bruns, *Planejamento e Otimização de Experimentos*, 2nd Edition, Unicamp, Brazil, 1996.
- [22] D.D. Dionysiou, M.T. Suidan, E. Bekou, I. Baudin, J.M. Lainé, *Appl. Catal. B: Environ.* 26 (2000) 153.
- [23] L. Sánchez, J. Peral, X. Doménech, *Electrochim. Acta* 42 (1997) 1877.
- [24] M.C. Yeber, J. Rodríguez, J. Freer, J. Baeza, N. Durán, H.D. Mansilla, *Chemosphere* 39 (1999) 1679.
- [25] K.P. Kringstad, K. Lindström, *Environ. Sci. Technol.* 18 (1984) 236A.
- [26] M.C. Yeber, J. Freer, M. Martínez, H.D. Mansilla, *Chemosphere* 41 (2000) 1257.

Paper 8

Photocatalyst-coated acrylic waveguides for oxidation of organic compounds

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PHOTOCATALYST-COATED ACRYLIC WAVEGUIDES FOR OXIDATION OF ORGANIC COMPOUNDS

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Abstract

Acrylic (polymethylmethacrylate) sheets were coated with a thin film of porous, titanium dioxide (TiO_2) semiconducting photocatalyst. The sheets were first passivated with a thin film of silica to prevent them from being oxidized by the TiO_2 semiconductor photocatalyst. The coated acrylic structures act as waveguides that propagate ultraviolet (UV) light in an Attenuated Total Reflection (ATR) mode. A recirculating reactor was used to evaluate the acrylic waveguides for their ability to photocatalytically oxidize formic acid in water. The TiO_2 -coated waveguides utilize activating ultraviolet light four times more efficiently for the photocatalytic oxidation of formic acid than TiO_2 films illuminated directly with diffuse UV light.

Introduction

Photocatalytic oxidation of organic contaminants on the surface of titanium dioxide (TiO_2) is an attractive process for remediating liquid or gas-phase waste streams. Organic compounds can be oxidized to carbon dioxide and water in the presence of TiO_2 , ultraviolet (UV) light (wavelength of ca. 380 nm or less), and an electron acceptor such as oxygen. This process occurs at room temperature. While the potential of TiO_2 photocatalysis for environmental remediation has generated considerable research interest (1), development of commercially viable systems has been hindered in large part by the expense of UV light generation and capture.

Conventional heterogeneous photocatalytic reactors are difficult to scale to the dimensions necessary for commercial applications because light is severely attenuated within the reactor through absorption or reflection by the catalyst, the reactant, reactor walls, and catalyst supports. Scaling-up of conventional photoreactors is also difficult and expensive because light intensity diminishes with the distance from the diffuse source. Since the rate of a heterogeneous photocatalytic reaction depends on the light intensity, a scaled-up photoreactor practically requires many light sources closely spaced throughout the reactor volume.

The use of waveguides to support and illuminate photocatalysts was initially proposed more than twenty years ago as a way to overcome the light distribution limitations inherent in conventional photoreactor designs (2). In a waveguide photoreactor, light enters the catalyst-coated waveguides (e.g. transparent optical fibers or planar structures) near the source where it is most intense, and it is distributed to the catalyst via successive internal reflections at the waveguide surface. Waveguide photoreactors would have several advantages in comparison to conventional photoreactor designs (e.g. packed bed or slurry reactors) in which the catalyst is directly illuminated by sunlight or artificial light. By capturing light from a single source and propagating it internally to the photocatalyst, waveguide reactors should increase the amount of fixed, illuminated catalyst per reactor volume. Furthermore, a waveguide photoreactor would more evenly distribute light from a diffuse source throughout the reactor volume.

Some researchers have coated silica optical fibers with TiO_2 in an effort to realize the advantages of waveguide supported photocatalysis for environmental remediation (3,4). While these efforts yielded photoreactors that successfully oxidized organic compounds, the TiO_2 -coated fibers that were developed did not propagate light effectively. Light was refracted out of the fibers at the TiO_2 -coated surface. At the Water Chemistry Program of the University of Wisconsin, we developed planar silica waveguides coated with TiO_2 that propagate UV light in an attenuated total reflection (ATR) mode (5). In an ATR mode, light propagates internally via successive total reflections at the waveguide boundaries. The TiO_2 coating absorbs a small portion of the light at each reflection. These systems do not lose light through refraction at the waveguide surface. We used these TiO_2 -coated waveguides to photocatalytically oxidize formic acid in water. A recent paper by Miller, et al. explains the optics of a low-refractive index substrate coated with a higher refractive index TiO_2 film (6).

While fused silica is an attractive waveguide medium because of its transparency in the UV spectrum, there are several practical limitations to using silica in commercial reactors. It is expensive, heavy (ca. 4 g/cm³), fragile, and difficult to machine. For this reason, we developed planar waveguides made from acrylic (polymethyl methacrylate) sheet. Acrylic is an attractive waveguide substrate because it is lighter than glass, easily machined, thermoformable and moldable. It can be formulated to be reasonably transparent in the near UV spectrum (transmittance = ca. 70% cm⁻¹ at wavelength = 360 nm), and an industry exists for the manufacture of UV-stable and transparent cell-cast acrylic sheet. Here we describe a process for coating acrylic sheet with a mesoporous TiO₂ film. The acrylic waveguides are passivated with a microporous silica film, and the TiO₂ is deposited on top of the silica. The silica film protects the acrylic from photooxidation by the TiO₂ semiconductor photocatalyst. We evaluate the waveguides' photocatalytic performance, and propose a reactor design that demonstrates the advantages of TiO₂-coated acrylic waveguides for the scale-up of TiO₂-based photocatalytic processes.

Experimental

Acrylic sheet (thickness = ca. 0.32 cm) was obtained from Cyro Industries (cat. no. AE-OP4). All chemicals were obtained from Aldrich Chemical Co. (Milwaukee, WI). Laboratory grade water (18 MΩ cm⁻¹) was generated with a Barnstead system.

The sol-gel synthetic method was used to prepare a colloidal silica sol. Tetra-ethyl orthosilicate was hydrolyzed in water and KOH (7). The resulting sol is composed of silica particles of ca. 3 nm in diameter and has a pH of ca. 9.5. The particles have a zeta potential of ca. 4.0. The pH of the silica sol was adjusted to ca. 3.5 by addition of 1 wt. % nitric acid in water.

Acrylic waveguides were prepared by cutting acrylic sheet to the desired dimensions. The waveguide edges were sanded with successively finer grained sandpaper (finished with 1000 grit paper). The edges were then polished with 45 μm diamond slurry on a polishing wheel. To prepare the acrylic waveguides for coating with silica and then TiO₂, they were first saponified in 5M NaOH for 1 hr., rinsed in water and air-dried. This step was necessary to make the acrylic surface hydrophilic. A microporous silica film was deposited onto the saponified acrylic waveguides by dipping them into the silica sol and withdrawing at a controlled rate of 2.5 cm/min followed by drying in air. The thickness of the silica film was adjusted by repeating the coating process. For the waveguides used in this study, three layers of silica were applied.

A mesoporous TiO₂ film was then deposited onto the silica-passivated acrylic by dipping the waveguides into a colloidal TiO₂ sol of pH = ca. 3.5 (8). The withdrawal rate was ca. 8 cm/min. TiO₂ films prepared from this method have a high surface area (>150 m² g⁻¹) and a pore radius of ca. 1.5 nm to 4 nm (8). These films have been shown to be effective photocatalysts (9). Six layers of TiO₂ were coated onto the waveguides. After coating, the edges were repolished to remove any TiO₂ or silica.

Profilometry measurements (Tencor, model 2000) made on equivalently coated glass plates were used to estimate the thickness of the silica and TiO₂ films. The films were inspected visually and with an optical microscope to determine their uniformity. SEM micrographs were obtained with a LEO model 952 scanning electron microscope.

An internal reflection photoreactor described in a recent paper was used to evaluate the TiO₂-coated acrylic waveguides for degradation of formic acid in water (5). A schematic of the reactor is shown in Figure 1.

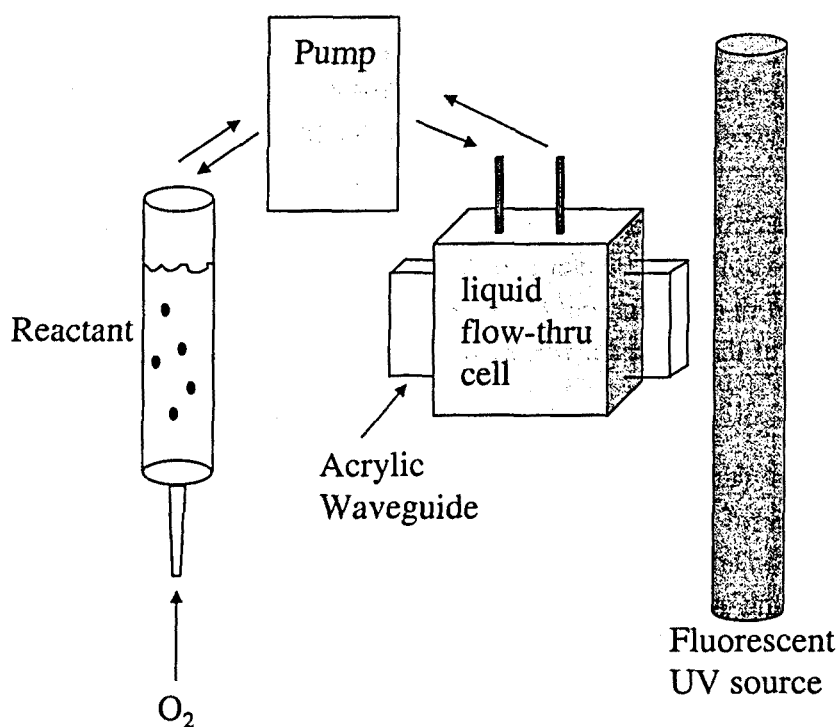


Figure 1. Schematic of recirculating photoreactor. The reactor was used to evaluate TiO₂/silica-coated acrylic waveguides for the photocatalytic oxidation of formic acid in water.

With this reactor, a rectangular acrylic waveguide measuring 5 cm x 2 cm x 0.3 cm was held in a flow-through liquid cell. A solution of 0.001 M formic acid in water was recirculated from an oxygenated reservoir across the TiO₂-coated face of the waveguide at a rate of 4 mL/min. The geometric surface area of the TiO₂ film exposed to the reactant was ca. 7.1 cm². Solution volume measured 10 mL. A fluorescent bulb (Sylvania, model F8T5350blb) positioned ca. 0.5 cm from the polished waveguide edge provided UV illumination. UV light intensity (all wavelengths < 400 nm) incident on the polished waveguide edge was measured with a radiometer (International Light, model no.). Formic acid concentration was measured using a Total Organic Carbon (TOC) analyzer (Shimadzu, model TOC5000). Measurements were made at the beginning of each experiment and after 4 hours of reactor operation.

The reactor was modified to allow light to shine on the directly onto the surface of the TiO₂-coated acrylic waveguides. This modification allowed comparisons between reaction rates for TiO₂ films illuminated by internally reflected light and for films illuminated directly. Light entered this modified flow-through reactor through the acrylic support and illuminated the TiO₂ film that contacted the formic acid solution. Lamp position was adjusted to make the intensity of the light striking the TiO₂ film roughly equivalent to that striking the waveguide edge in the above-described series of experiments. TiO₂ film thickness was the same in both sets of experiments and the same geometric surface area of TiO₂ was allowed to contact the reactant. The reactant solution was 15 mL of 0.001 M formic acid in water. Experiment duration was 25 minutes.

In both sets of experiments, the reactor was operated without illumination, and no degradation was observed. Flow rates were varied with no apparent change in reaction rates. For both sets of experiments (internally propagated light and direct illumination of the TiO₂), three samples were evaluated in the reactor, and the experiment was repeated three times for each sample. The change in concentration with time was used to calculate an absolute rate of reaction adjusted for geometric TiO₂ surface area for each sample (reported in units of mol s⁻¹ cm⁻²).

Results and discussion

Upon visual examination, the TiO₂ and silica films have few observable defects. The coated waveguides exhibit birefringence to visible light, indicating that the films are transparent with boundaries parallel to the acrylic surface. Gentle abrasion of the waveguides when they were immersed in water did not remove the films, indicating reasonable adhesion. However, exposure of the waveguides to methanol, acetone or other solvents that attack

acrylic removed the films. No film delamination was observed during operation of the test reactor.

Profilometry performed on equivalently coated glass plates showed a thickness of 50-100 nm for the silica films and 350-400 nm for the TiO₂ films. SEM analysis of the coated acrylic waveguides showed similar film thicknesses.

The highest quality silica films were obtained when the colloidal silica sol used to coat the waveguides was adjusted to pH=3.5. At this pH, the surface charge of the silica particles is neutral or slightly negative (7). If one assumes that the saponified surface of the acrylic has a pK_a value similar to that of acrylic acid (pK_a=ca. 4.2), then the surface of the acrylic is protonated at this pH. We suspect that these conditions allow for favorable film deposition and adhesion. A schematic of the TiO₂/silica-coated acrylic is shown in Figure 2.

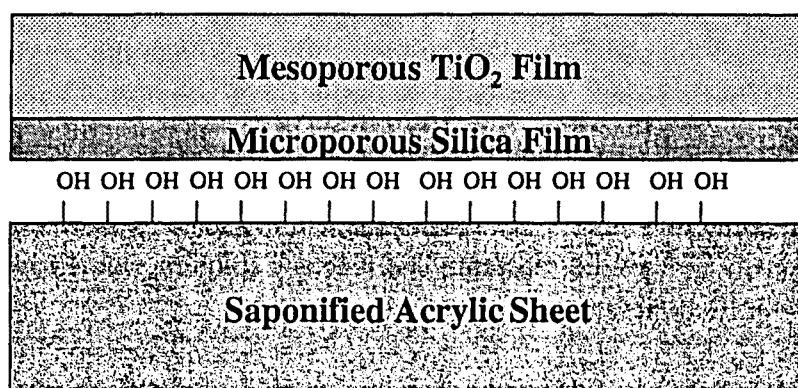


Figure 2. Schematic of TiO₂/silica-coated acrylic waveguide. Saponification of the acrylic sheet with 5M NaOH replaces surface methyl groups with hydroxyl groups.

When the recirculating photoreactor was operated in internal reflection mode, the concentration of the 0.001 M formic acid solution was reduced by $36 \pm 4\%$ in 4 hours of reaction time. Light intensity striking the waveguide edge measured 12 ± 1 mW/cm². The reaction rate normalized to the geometric surface area of TiO₂ film exposed to the reactant was calculated using the following relation:

$$r = \frac{C_0 \times X \times V}{t \times A};$$

where r is the area-adjusted reaction rate ($\text{mol s}^{-1} \text{cm}^{-2}$), C_0 is the initial concentration of the reactant solution (mol/L), X is the fractional conversion of the reactant, V is the reactant solution volume (L), t is the reaction time (seconds), and A is the geometric surface area of TiO_2 film exposed to the reactant (cm^2). The calculated rate of formic acid oxidation for the $\text{TiO}_2/\text{silica}$ -coated acrylic waveguides was $3.5 \pm 0.4 \times 10^{-11} \text{ mol s}^{-1} \text{cm}^{-2}$.

For the $\text{TiO}_2/\text{silica}$ -coated acrylic illuminated directly with the same UV light intensity, the overall formic acid degradation measured $43 \pm 2\%$ in 25 minutes of reaction time. This was equivalent to a rate of $6.0 \pm 0.3 \times 10^{-10} \text{ mol s}^{-1} \text{cm}^2$.

Under the conditions of the experiment, it appears that the TiO_2 coating is ca. 17 times more effective when illuminated directly rather than by light propagated internally through the waveguide support. However, this apparent advantage is negated when one considers that a much greater geometric surface area of TiO_2 could potentially be illuminated in a reactor consisting of an array of TiO_2 -coated acrylic waveguides. This difference is illustrated in Figure 3.

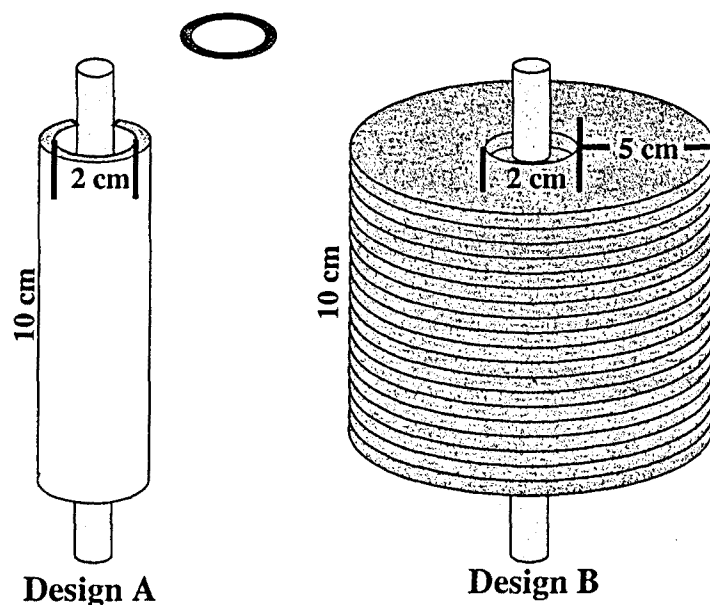


Figure 3. Schematics of two equivalently illuminated TiO_2 photoreactors. Design A is an annular design where the light is directly incident on the TiO_2 film. The geometric surface area of illuminated catalyst = ca. 63 cm^2 . Design B incorporates an array of 20 $\text{TiO}_2/\text{silica}$ -coated acrylic waveguides spaced 0.2 cm apart. Each waveguide is ca. 0.3 cm thick and has a geometric surface area of 220 cm^2 . The total illuminated catalyst surface area = ca. 4400 cm^2 .

An annular reactor design, as specified in Figure 3 Design A, wherein the TiO₂ film is illuminated directly by a cylindrical UV source (e.g. a fluorescent UV bulb) would have ca. 63 cm² of illuminated catalyst. However, an array of coated waveguides as configured in Design B would have an illuminated, geometric catalyst surface area of ca. 4400 cm². Thus a far greater amount of TiO₂ catalyst can be illuminated in the waveguide reactor design than in the annular design. In fact, the waveguide design should be ca. 4 times more effective at degrading formic acid under identical conditions of illumination.

We have shown that a mesoporous, photocatalytic TiO₂ film can be securely attached to acrylic sheet. Furthermore these coated acrylic structures will act as waveguides and can be used to photocatalytically oxidize organic compounds. These waveguides can be incorporated into photoreactor designs to dramatically increase the amount of catalyst that can be illuminated with a single light source. This should aid the scale-up of photocatalytic systems to the dimensions required for commercial applications. Additionally, acrylic waveguides can be easily machined into a variety of geometries, thereby reducing manufacturing costs and allowing greater freedom in the design of heterogeneous photocatalytic reactors.

References

- 1) Blake, D.M. Bibliography
- 2) Marinangeli, R.E.; Ollis, D.F. *AIChE J.* **1977**, *23* (4), 1000.
- 3) Bauer, R.; Hofstadler, K. *Environ. Sci. Technol.* **1994**, *28*, 670.
- 4) Peill, N.J.; Hoffmann, M.R. *Environ. Sci. Technol.* **1995**, *29*, 2974.
- 5) Miller, L.W.; Tejedor-Tejedor, M.I.; Anderson, M.A. *Environ. Sci. Technol.*
- 6) Miller, L.W.; Tejedor-Tejedor, M.I.; Nelson, B.P.; Anderson, M.A. *J. Phys. Chem. B*
- 7) Chu, L.; Tejedor-Tejedor, M.I.; Anderson, M.A. *Mater.Res. Soc. Symp. Proc.* **1994**, *346*,
Materials Research Society
- 8) Xu, Q.; Anderson, M.A. *J. Mater. Res.* **1991**, *6* (5), 1073.
- 9) Aguado, M.A.; Anderson, M.A. *Solar Energy Materials and Solar Cells* **1993**, *28*, 345.

Paper 9

Removal of organic contaminants in textile mill effluents by Fenton and Photo-Fenton reactions

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REMOVAL OF ORGANIC CONTAMINANTS IN TEXTILE MILL EFFLUENTS BY FENTON AND PHOTO-FENTON REACTIONS

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Abstract

Treatment of textile wastewaters from hydrogen peroxide bleaching process by using Fenton reagent and irradiation, which provides the occurrence of Fenton and Photo-Fenton reactions, is investigated. A high TOC reduction and low cost treatment is obtained, by using solar irradiation as light source. Moreover, the importance of key parameter temperature during the Fenton and Photo-Fenton reaction is shown.

Introduction

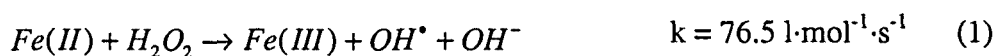
The chemical and biological treatments traditionally applied to wastewaters from the textile industry are not capable to mineralize the large quantities of organic matter present in these kinds of effluents [1-2]. Furthermore, treatment cost of textile wastewaters has been scaling rapidly in recent years. Researchers have firmly focussed in the study of more cost-effective treatment methods [2].

Due to the high level of contamination of the effluent, a hydrolysis in basic media was carried out before the application of the treatments. Dorica has reported the removal of organic chlorine from bleach paper plant effluents using alkaline hydrolysis [3]. Also, Milosevich et.al [4] demonstrated that neutralization of bleach paper effluent with lime mud, followed by the addition of alkaline sulphide process liquor was a practical, cost-effective method of reducing mill AOX (adsorbable organic halogen) discharge. In other studies of the research group same results were obtained [5,6].

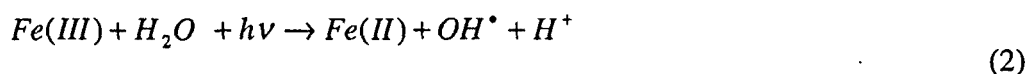
It is increasing the number of research groups who applied Advanced Oxidation Processes (AOP's) for pollutant degradation due to the high oxidative power (2.8 V vs. NHE) of the OH radical. The most widely known AOP's include: heterogeneous photocatalytic oxidation [7-12], treatment with ozone (often combined with H₂O₂, UVA, or both) [2, 13-19], H₂O₂/UV systems [20,21], Fenton [21-23] and Photo-Fenton type reactions [24-26].

The AOP's common problems are high electrical energy demand and/or excessive consumption of chemical reagents [27]. Fortunately, Photo-Fenton reaction can be driven with low energy photons in the visible part of the spectrum. Thus, Photo-Fenton processes are a potentially low cost AOP that can be run under solar irradiation [26].

According to the classic mechanism proposed by Haber and Weiss [28], the hydroxyl radicals $\text{OH}\cdot$ generated in the Fenton reaction are produced by interaction of H_2O_2 with ferrous salts:



The rate of degradation of the organic pollutants by Fenton reaction could increase when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photoreduction of Fe (III) to Fe(II) ions; a step that produces new $\text{OH}\cdot$ radicals and regenerates Fe(II) ions that can further react with more H_2O_2 molecules. The photoreduction of Fe (III) follows the equation:



However, new studies have presented evidence of some lacks in reactions (1) and (2). Also, it has been established the formation of alternative oxidant in place of, or more likely in addition to, $\text{OH}\cdot$ [29,30].

The main literature sources and several studies in our research group [26,31] demonstrate that Fenton and Photo-Fenton reactions are pH dependent processes. A pH around 3 allowed faster and higher TOC removal. Thus, all of the experiments presented in this study were performed at pH 3.

Spectrophotometric analyses of the effluent were performed throughout to determine the kind of compounds present in the studied effluent. We found aromatic compounds, linear acids, and others, which are typical compounds named in the textile references consulted [32,33]

The purpose of this study is the oxidation of the organic compounds present in a typical bleaching textile mill effluent, by Fenton and Photo-Fenton reactions, in order to achieve the highest reaction yields with the lowest cost treatment. The role that several experimental parameters like temperature and light source have on the treatment cost will be examined.

Experimental

Effluent and reagents

The effluent used in the present research was obtained from the hydrogen peroxide step of a bleaching sequence with previous hypochlorite pretreatment, applied to cotton mixed with a very low portion of synthetic fibers that was supplied by a Spanish textile manufacturer. In order of working with lower levels of organic contaminant load, hydrolysis with $\text{Ca}(\text{OH})_2$ (pH 12, during 1 h) is carried out to the above mentioned effluent. This process was carried out at room temperature following that indicated in [3].

The rest of the chemicals used were, at least, of reagent grade. Analytical grade hydrogen peroxide and heptahydrated ferrous sulfate were purchased from Panreac, and were used as received. Solutions were prepared with de-ionized water obtained from a Millipore Mili-Q system.

Experimental procedure

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm³ capacity. The reaction mixture inside the cell, consisting of 100 mL of organic effluent and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar; temperature was maintained at $\pm 0.1^\circ\text{C}$. Solar and Xe lamp irradiation were used as light sources.

Analytical methods

Total organic carbon (TOC) of initial and irradiated samples was determined with a Shimadzu 5000 TOC analyzer. Color determination was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells and referenced to a Pt-Co standard solution, according to standard H.5 of the CPPA [34]. Chemical Oxygen Demand (COD) was determined by standardized methodology (EPA 00340).

For the analysis of low molecular weight compounds dissolved in the effluent, a HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector was used. The GC-MS analysis was carried out with ionization of electronic impact, 70 eV and the spectra were recorded in the interval 40 – 600 amu.

One liter of the sample was filtered with Speedisk[®] membrane (J.T. Baker) following the EPA 525 procedure. Identifications were carried out with the aid of the data base library WILEY (275,000 spectra) and NIST (130,000 spectra) and with a customized database generated in the UAB laboratory. A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with the following dimensions 30 m, 250 μm , 0.25 μm was used. The carrier was helium with linear speed of 42 $\text{cm}\cdot\text{s}^{-1}$. The temperature program used during the GC-MS analysis ramped as follows: 70 $^{\circ}\text{C}$ (3 min), 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ until 270 $^{\circ}\text{C}$ (30 min). The sample injection was carried out with a 0.6 min of splitless time, at 250 $^{\circ}\text{C}$. The carrier gas flow rate in the GC was 1.3 $\text{mL}\cdot\text{min}^{-1}$.

Results and discussion

Table I shows the global parameters values of the textile effluent after hydrolysis.

Table I.- Initial characterization parameters of textile effluent after hydrolysis

Parameter	Value
TOC (ppm)	605 \pm 9*
COD ($\text{mg}\cdot\text{L}^{-1}$ O ₂)	1669 \pm 4*
Color ($\text{mg}\cdot\text{L}^{-1}$ Pt)	40 \pm 8*

*(n = 4, α = 0.05)

As can be seen, TOC and COD have high values in comparison with color, which complies environmental legislation [35]

A qualitative analysis of the effluent by GC-MS allows determination of the structure of some low molecular weight compounds present in the initial effluent. The identified compounds are shown in Table II. All the substances found were in concordance with the ones reported by other authors [33, 36-39] who suppose these compounds are mainly coming from the degradation of the surfactant during the bleaching step. Surfactant products are usually based in a nonylphenol and an unsaturated fat acid. Also a great number of unidentified compounds appear in the chromatogram, which are not shown here.

Table II.- Initial compounds found by GC-MS in the textile effluent after hydrolysis

Compound	Retention time	Reliability
Aromatic compounds		
benzoic acid	10.80	97 %
benzeneacetic acid	12.90	76 %
3-methyl benzoic acid	13.72	94 %
ethyl ester 4-ethoxy- benzoic acid	19.32	96 %
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	24.70	98 %
Linear acids		
nonanoic acid	13.60	95 %
decanoic acid	16.27	96 %
undecanoic acid	19.13	96 %
dodecanoic acid	20.70	99 %
tetradecanoic acid	24.80	98 %
pentadecanoic acid	26.80	97 %
hexadecanoic acid	29.10	99 %
heptadecanoic acid	30.76	96 %
octadecanoic acid	32.62	93 %
Other compounds		
2,2'-oxybis-ethanol	5.30	83 %
decane	5.48	91 %
2,8-dimethyl-4-methylene-nonane	7.73	86 %
2-decanone	10.71	90 %
methyl ester nonaic acid	17.80	70 %
2-butyl octanoic acid	19.30	91 %
2-propylnonanoic acid	19.35	72 %
2-methyl undecanoic acid	19.72	91 %

The intensity and the wavelengths emitted by the light source are key conditions when trying to describe the participation of the Photo-Fenton reaction. It is specially interesting, from the application point of view, the possibility of using solar light. In figure 1, similar behavior is observed in TOC removal when Xenon or solar light is used. In both experiments the ratio between reagents is 10 : 1; 1000 ppm of H₂O₂ per 100 ppm Fe (II).

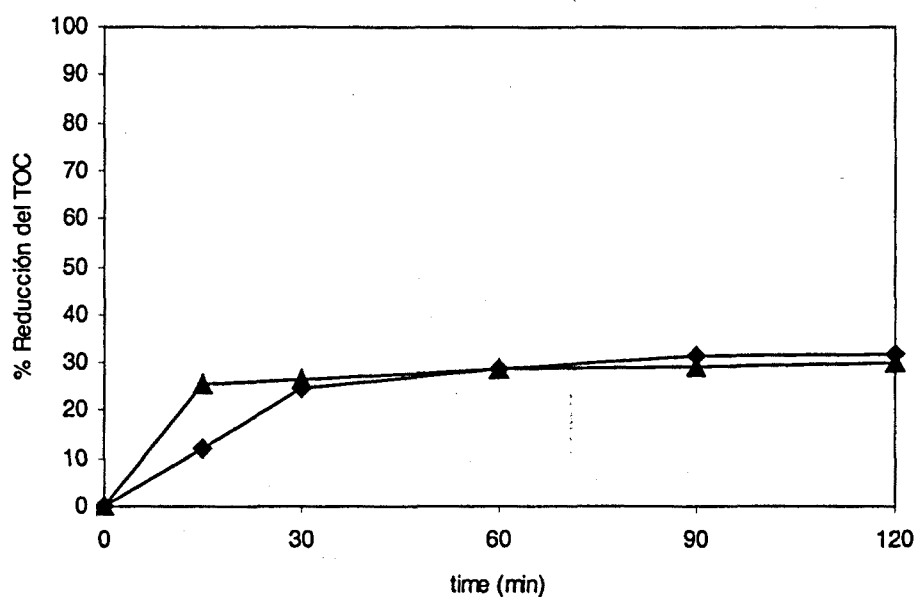


Figure 1. TOC decay vs. reaction time when using different light sources. Solar light (▲); Xe light (◆). $[H_2O_2]_0 = 1000$ ppm, $[Fe(II)]_0 = 100$ ppm, $pH = 3$, $T = 40^\circ C$.

Figure 1 shows clearly that the same tendency is followed with both light sources. Even during the first 15 minutes the sunlight seems to be more effective than the Xe lamp. In the following time both have similar behavior. Due to the experimental setup, the experiment with solar light was carried out at a single temperature, oscillating between 35 and 40 °C. The other one took place at 40°C. Thus, the large reduction of TOC accomplished in the experiments could be a consequence of both, the number of photons and the temperature. The aim of this comparison light sources is to make valid the conclusions obtained when the light source is a Xenon light in the case of carried out experiment under solar light irradiation. Previous studies in our research group found also that both light sources have same kind of irradiation and consequently cause same effect [31].

The beneficial effect of temperature was carefully tested in the set of experiments, where three different temperatures (25, 40 and 70 °C) were used in the dark and under irradiation of the Xe lamp. As a result, the decrease of organic concentration with time due to oxidative degradation of the textile bleach effluent by Fenton and Photo-Fenton reaction is shown in Figure 2.

The differences between the pairs of experiments carried out under the same conditions (irradiation or absence of light) are due to the different temperature used (25, 40 and 70 °C). From other side, for the six experimental conditions of figure 2, is expected a $t_{1/2}$ of Fe (II) disappearance of less than one second. This indicates that the Fenton reaction is completed in a very short time, due to the large rate of Fenton reaction relative to the

rate of the Photo-Fenton process, along with the limiting role played by the Fe(II) concentration.

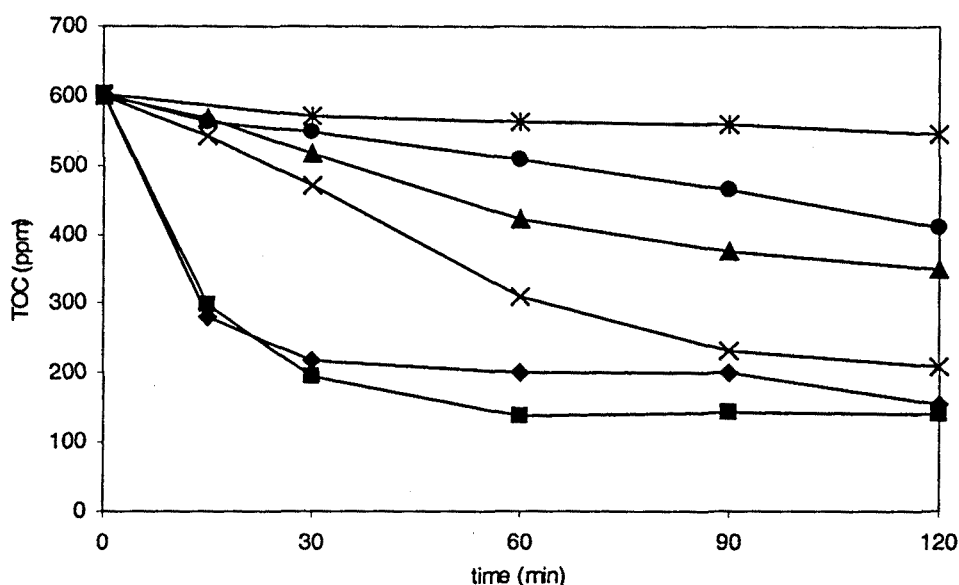
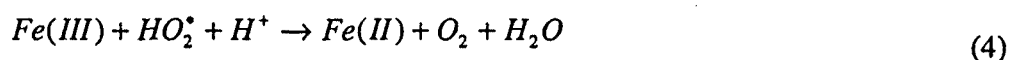
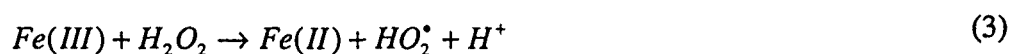


Figure 2. Effect of temperature on TOC removal. 25 °C in the dark (*); 25 °C under Xe lamp irradiation (●); 40 °C in the dark (▲); 40 °C under Xe lamp irradiation (X); 70 °C in the dark (◆); 70 °C under Xe lamp irradiation (■). $[H_2O_2]_0 = 10000$ ppm, $[Fe(II)]_0 = 100$ ppm, pH = 3.

Several reactions between Fe (III) and H_2O_2 related species can regenerate, even in the dark, Fe(II) and lead to a further degradation of organic matter after the initial Fe(II) has been consumed [20,26]:



The production of radicals by reaction between Fe(III) and H_2O_2 has been called Fenton-like reaction [20,26]. The regenerated Fe (II) can react with H_2O_2 with formation of more OH^* . With a larger initial H_2O_2 concentration, more Fe(II)/Fe(III) cycles can be completed and more organic matter can be destroyed. Under irradiation, the recovery of Fe (II) is even faster because of the Photo-Fenton reaction.

When the experiment was carried out at 70°C, levels of TOC removal over 65% were attained after just 30 minutes of reaction, both, in the dark and under irradiation. Thus, under a high temperature condition the system is so fast that not important differences arise between the Fenton and the Fenton-Photo-Fenton reactions. Since the 100 ppm of

Fe (II) cannot directly produce enough OH[·] radicals to account for the level of TOC removal, the acceleration of Fenton reaction with temperature is not the only cause such an observation. The temperature seems to be assisting alternative ways of H₂O₂ cleavage and OH[·] formation, or Fe (II) recovery. Blank experiments (data non showed) revealed that neither the irradiation nor the temperature can alone produce noticeable decreases of TOC, the simultaneous presence of Fe(II) and H₂O₂ being always necessary. It has to be said that, the experiment carried out at 25 and 40°C, levels of TOC removal improve under light irradiation. For higher temperature Photo-Fenton reaction has not showed any significant effect. Similar effects were observed when the research group was working with bleaching Kraft mill effluents [31].

The increase of TOC removal in the experiment carried out under Xenon light source (comparable with solar irradiation) and with higher temperature can be translated in a reduction of the cost treatment as figure 3 shows:

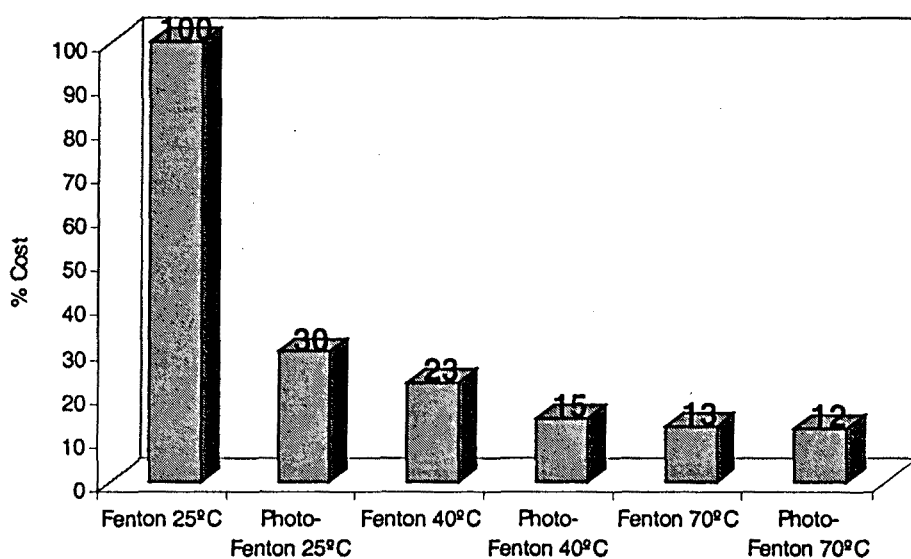


Figure 3. *Relative cost of the Fenton and Photo-Fenton treatments. The calculations are referred to the Fenton treatment carried out at 25 °C.*

All the prices used to make this comparative economic study have been taken from the laboratory scale, and were done under the two following premises:

- The light source cost is cancelled due to Xenon irradiation gives same results as solar light.
- It is not taken in account the energy necessary for the increasing of the temperature of the wastewater because it is important to remark that in

comparison to most industrial wastewaters, the temperature of textile effluents is unusually high. During the dyeing process, rinse waters of up to 90 °C are used in various steps. The near 40°C temperature of the textile wastewaters is attributable to the hot rinse waters [2].

This economic study at laboratory scale is enough reliable to compare how Fenton and Photo-Fenton reactions could be improved in order to save time and decrease cost. It is clearly shown that it is possible an important reduction of the cost treatment without sacrifice in TOC removal.

Conclusions

The degradation of the organic content of a bleaching textile effluent has been successfully carried out by simultaneously applying Fenton and Photo-Fenton reactions. The most significant effect was ascribed to solar light source. In only 2 hours of reaction it is possible to reduce 70 % the cost of the treatment when solar irradiation allowed Photo-Fenton reaction to be taken place. Consequently, solar light is an efficient and economical source of irradiation.

From the data, it is clear that temperature is the other particularly significant factor for increasing TOC removal even without light irradiation, just Fenton reaction. A decrease of 77% in the cost is possible just increasing temperature from 25°C to 40°C. Temperature is a key parameter that has to be taken into account, specially for those applications where TOC removal rate can be increased by using low cost heat (heat exchangers, co-generation, etc.).

The simultaneous effect of use solar irradiation and increase temperature condition allowed the treatment cost be reduced 88 % for an efficient TOC reduction.

Successful TOC removal join to reduce cost treatment put the combination of Fenton and Photo-Fenton processes in a pole position inside the every time more applied AOP's.

References

1. Tzitzis, M.; Vayenas, D.V., Lyberatos, G., (1994) *Wat. Sci. Tech.*, **29** , 151.
2. Lin, S.H., Peng, C.H.F., (1994) *Wat. Res.*, **28** , 277.
3. Dorica, J. (1992) *J. Pulp Paper Sci.*, **18** , 231.
4. Milosevich, G.M., Hill, D.A., (1992) *Pulp Pap. Canada*, **93** , 61.
5. Pérez; M., Torrades, F., Domènech; X., Peral, (1997), *J. Química Analítica*, **16** , 211.
6. Torrades, F., Peral, J., Pérez, M., Domènech, X., Garcia Hortal, J.A., Riva, M.C. (2001), *Tappi Journal*, **84** , 63.
7. Hoffmann, M.R., Martin S.T., Choi, W., Bahnemann, D.W., (1995) *Chem.Rev.*, **95** , 69.
8. Ollis, D.F., (1991) in *Photochemical Conversion and Storage of Solar Energy*, (Pelizzetti, E., and Schiavello, M., ed.), Kluwer, Dordrecht.
9. Linsebigler, A.L., Lu, G., Yates, J.T., (1995) *Chem. Rev.*, **95** , 735.
10. Fox, M.A., Dulay, M.T., (1993) *Chem.Rev.*, **93** , 341.
11. Pérez, M., Torrades, F., García Hortal, J.A., Domènech, X., Peral, J., (1997) *J. Photochem. Photobiol. A: Chem.*, **109** , 281.
12. Mills, A., Le Hunte, S., (1997), *J. Photochem. Photobiol. A: Chem.*, 1081.
13. Saunamäki, R., Sorvari, J., (1992) *Nordic Pulp and Paper Research Journal*, **3** , 113.
14. Sánchez, L., Peral, J., Domènech, X., (1998) *Appl. Catal. B: Environ.*, **19** , 59.
15. Tanaka, K., Abe, K., Sheng, C.Y., Hisanaga, T., (1992) *Environ. Sci. Technol.*, **26** , 2534.
16. Tanaka, K., Abe, K., Hisanaga, T., (1996) *J. Photochem. Photobiol. A: Chem.*, **101** , 85.
17. Muller, T.S., Sun, Z., Kumar, G., Itoh, K., Murabayashi, M., (1998) *Chemosphere*, **36** , 2043.
18. Klare, M., Waldner, G., Bauer, R., Jacobs, H., Broekaert, J.A.C., (1999) *Chemosphere*, **38** , 2013.
19. Logager, T., Holcman, J., Sehested, K., Pedersen, (1992) *Inorg. Chem.*, **31** , 3523.
20. Pignatello, J., (1992) *Environ. Sci. Technol.*, **26** , 944.
21. Peyton, G.R., (1990) in *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, 313, Lewis Publishers, Chelsea.
22. Chamorro, E., Marco, A., Esplugas, S., (2001), *Water Research*, **35** , 1995.
23. Ruppert, G., Bauer, R., Heisler, G., (1993) *J. Photochem. Photobiol. A: Chem.*, **73** , 75.
24. Kiwi, J., Pulgarin, C., Peringer, P., (1994) *Appl. Catal. B: Environ.*, **3** , 335.
25. Tang, W.Z., Huang, C.P., (1996) *Environ. Technol.*, **17** , 1371.
26. Safarzadeh-Amiri, A., Bolton, J.R., Cater, S.R., (1996) *J. Advan. Oxid. Technol.*, **1** , 1.
27. Bauer, R., Fallmann, H., (1997) *Res. Chem. Intermed.*, **23** , 341.
28. Haber, F., Weiss, J., (1934) *J. Proc. R. Soc. London, Ser. A*, **147** , 332.
29. Bossmann, S. H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E. P., Payawan, Jr., L., Straub, M., Wörner, M., Braun, A. M., (1998) *J. Phys. Chem. A*, **102** , 5542.
30. Pignatello, J. J., Liu, D., Huston, P., (1999) *Environ. Sci. Technol.*, **33** , 1832.
31. Pérez; M., Torrades, F., Garcia-Hortal, J.A., Domènech; X., Peral, J. Submitted to *Appl. Catal. B Environ.*

32. Janitza, J., Koscielski, S., Krautter, A., (1994) *Textil Praxis International*. WURSTER
33. Lopez, D., (1999) *thesis*, UPC, Terrassa, Spain.
34. Canadian Pulp and Paper Association Standard Method H.5 – *Color of Pulp Mill Effluents*
(Approved method, December 1991; Revised, August 1993).
35. Lescot, J.C., Jappinen, H., (1994) *Appita J.*, 47 , 330.
36. Matthigs, E., Hennes, E.C. (1991) *Tenside Surf.Det.*, 28, 22.
37. Rivera, J., Caixach, J., Figueres, A., Fraisse, D., Ventura, F., (1988) *Biochemical and Environmental Mass Spectrometry*, 16, 403.
38. Ventura, F., Figueres, A., Caixach, J., Espadales, I., Romero, J., Guardiola, J., Rivera, J.,
(1988) *Water Res.*, 22, 1211.
39. Walhberg, C., Renberg, L., Wideqvist, U., (1990) *Chemosphere*, 20, 179.

Paper 10

Fenton and Photo-Fenton oxidation of textile effluents

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Abstract

The simultaneous use of Fenton reagent and irradiation for the treatment of textile wastewaters generated during a hydrogen peroxide bleaching process is investigated. The experimental conditions tested during this study provide the simultaneous occurrence of Fenton, Fenton-like and photo-Fenton reactions. The batch experimental results are assessed in terms of TOC reduction. Identification of some of the chemical constituents of the effluent was performed by means of GC-MS. Other pollution related features of the initial effluent like COD and color were also measured. The main parameters that govern the complex reactive system, i.e., light intensity, temperature, pH, Fe(II) and H₂O₂ initial concentrations have been studied. Concentrations of Fe(II) between 0 and 400 ppm, and H₂O₂ between 0 and 10000 ppm were used. Temperatures above 25 °C and up to 70 °C show a beneficial effect on organic load reduction. A set of experiments was conducted under different light sources with the aim to ensure the efficiency of using solar light irradiation. The combination of Fenton, Fenton-like and photon-Fenton reactions has been proved to be highly effective for the treatment of such a type of wastewaters, and several advantages for the technique application arise from the study.

Keywords: Advanced Oxidation Processes, Fenton, Photochemical reactions, Textile.

Introduction

The textile industry produces large volumes of bleaching effluents that contain appreciable quantities of organic compounds which are not easily amenable to chemical or biological treatment [Tzitzzi, M., et al. (1994). Lin, S.H. and Peng, C.F. (1994)]. Furthermore, treatment cost of textile wastewaters has been scaling rapidly in recent years. Hence a search for more cost effective treatment methods has practical application [Lin, S.H. and Peng, C.F. (1994)].

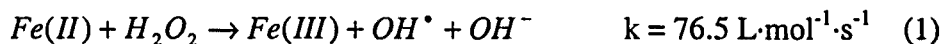
Most of the textile effluents have high levels of DQO, and hydrolysis in basic media is often carried out before the application of other treatments. Dorica [Dorica, J. (1992)] has reported the removal of organic chlorine of bleach paper plant effluents using alkaline hydrolysis. Pérez et al. [Torrades, F., et al. (2001)] have carried out studies where similar results were obtained.

Recently, chemical treatment methods, based on the generation of hydroxyl radicals, known as Advanced Oxidation Processes (AOPs), have been applied for pollutant degradation, due to the high oxidative power of the OH radical. The most widely studied AOPs include: heterogeneous photocatalytic oxidation [Hoffmann, M.R., et al. (1995). Linsebigler, A.L., et al. (1995). Pérez, M., et al. (1997). Mills, A. and Le Hunte, S. (1997)], treatment with ozone (often combined with H₂O₂, UVA, or both) [Sánchez, L., et al. (1998). Tanaka, K., et al. (1996). Muller, T.S., et al. (1998). Klare, M., et al. (1999). Logager, T., et al. (1992)], H₂O₂/UV systems [Peyton, G.R. (1990)], Fenton [Peyton, G.R. (1990). Chamarro, E., et al. (2001). Ruppert, G., et al. (1993)] and Photo-Fenton type reactions [Pignatello, J.J. (1992). Kiwi, J., et al. (1994). Tang, W.Z. and Huang, C.P. (1996). Safarzadeh-Amiri, A., et al. (1996). Bauer, R. and Fallmann, H. (1997)].

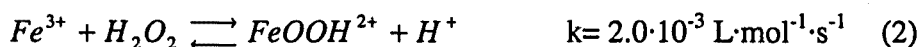
The high electrical energy demand or the consumption of chemical reagents are common problems among all the AOPs [Bauer, R. and Fallmann, H. (1997)]. Specially, the production of photons with artificial light sources require an important energy input. However not all photoassisted processes require light with the same wavelength and energy. While direct O₃ or H₂O₂ photolysis need photons of short wavelength (<310 nm), TiO₂ photocatalysis can take advantage of photons of wavelengths up to 380 nm [Hoffmann, M.R., et al. (1995)], and photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures Fe(III) + H₂O₂ (known as Fenton like reactions [Pignatello, J.J. (1992)]) have shown photon absorption up to 550 nm [Sun, Y. and Pignatello, J.J. (1993). Pignatello, J.J., et al. (1999)]. In presence of Fenton reagent photochemical reactions can be driven with photons of low energy, photons that belong to the visible part of the spectrum. Thus, Photo-Fenton processes are a potential cost-

reduced AOP that can be run under solar irradiation [Safarzadeh-Amiri, A., et al. (1996)].

In the generally accepted mechanism of Fenton reaction hydroxyl radicals $\text{OH}\cdot$ are produced by interaction of H_2O_2 with ferrous salts



Fe(III) can react with H_2O_2 in the so-called Fenton like reaction:



regenerating Fe(II) and thus, supporting the Fenton process [Pignatello, J.J. (1992)].

The rate of degradation of the organic pollutants by Fenton reaction could increase when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photoreduction of Fe(III) to Fe(II) ions, a step that produces new $\text{OH}\cdot$ radicals and regenerates Fe(II) ions that can further react with more H_2O_2 molecules. The photoreduction of Fe(III) follows the equation:



with Fe(OH)^{2+} being the dominant Fe(III) species in solution at pH 2-3. Recently, it has been proven that the irradiation of $\text{Fe(III)} + \text{H}_2\text{O}_2$, also called photo-Fenton reaction, enhances the reaction rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to organic matter [Pignatello, J.J., et al. (1999). Bossmann, S.H., et al. (1998)]. Absorption of visible light by the complex formed between Fe(III) and H_2O_2 seems to be the cause of formation of such high valence Fe-based oxidants.

In the present paper we have undertaken the study of the oxidation of the organic compounds present in a bleaching textile effluent by Fenton and Photo-Fenton reactions, in order to establish the efficiency of both AOP for the treatment of such wastewaters. The role that several experimental parameters like temperature, light intensity, and reagent concentration have on the reaction yields have been examined.

Experimental

The effluents used in the present research were obtained from the hydrogen peroxide bleaching sequence of a cotton substrate mixed with a very low portion of synthetic fibers and pretreated with hypochlorite. The wastewater was supplied by a Spanish textile manufacturer. In order to work with lower level of organic pollutants, hydrolysis with $\text{Ca}(\text{OH})_2$ (pH 12, room temperature, during 1 h) was carried out to the effluent, following the procedure of Dorica [Dorica, J. (1992)].

The rest of the chemicals used were, at least, of reagent grade. Analytical grade hydrogen peroxide and heptahydrated ferrous sulfate were purchased from Panreac and Aldrich, respectively, and were used as received. Solutions were prepared with deionized water obtained from a Millipore Mili-Q system.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm³ capacity. The reaction mixture inside the cell, consisting of 100 ml of organic effluent and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. During most of the experiments the temperature was maintained at $25.0 \pm 0.1^\circ\text{C}$. A 6 W Philips black-light fluorescent lamp and a 250 W xenon lamp (Applied Photophysics) were used as light source. The IR fraction of the xenon light beam was removed by the water in the double jacket of the photoreactor. The intensity of the incident light inside the photoreactor, measured employing a uranyl actinometer, was $1.38 \cdot 10^{-9}$ Einstein $\cdot\text{s}^{-1}$ for the fluorescent lamp and $7.55 \cdot 10^{-8}$ Einstein $\cdot\text{s}^{-1}$ for the xenon lamp.

Total organic carbon (TOC) of initial and irradiated samples was determined with a Shimadzu 5000 TOC analyzer. Color determination of the initial sample was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells, according to standards H.5 of the CPPA [Canadian Pulp and Paper Association (1993)].

Identifications of some chemical constituents of the wastewater was attempted by means of GC-MS. A HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector was used. The GC-MS analysis was carried out with ionization of electronic impact, 70 eV, the spectra were recorded in the interval 40 – 600 amu.

One liter of the sample was filtered with Speedisk[®] membrane (J.T. Baker) following the EPA 525 procedure. Samples were reconstituted to 100 μL in dichloromethane and 1 μL was injected in the GC. Identifications were carried out with the aid of the data base library WILEY (275,000 spectra) and NIST (130,000 spectra).

A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with dimensions of 30 m, 250 μm , 0.25 μm was used. The carrier gas flow rate in the GC was 1.3 $\text{mL}\cdot\text{min}^{-1}$. The sample injection was carried out with a 0.6 min of splitless time, at 250 $^{\circ}\text{C}$. The temperature program used during the GC-MS analysis ramped as follows: 70 $^{\circ}\text{C}$ (3 min), 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ until 270 $^{\circ}\text{C}$ (30 min).

Results and discussion

After hydrolysis the textile effluent have the following global parameters values: $605 \pm 9^*$ $\text{mg} \cdot \text{L}^{-1}$ of TOC; $1669 \pm 4^*$ $\text{mg} \cdot \text{L}^{-1}$ O_2 of COD; and $40 \pm 8^*$ $\text{mg} \cdot \text{L}^{-1}$ Pt of color, $^*(n = 4, \alpha = 0.05)$.

Table 1 contains the compounds that have been identified by GC-MS. Several of these compounds can be considered degradation products of nonylphenol derivatives, often used as surfactant in the preparation of textile fibers. Also, a large number of unidentified compounds appear in the chromatogram, although they are not included in table 1.

As expected from equations 1 to 5 the complex reactive system is a pH dependent processes. However, each reaction has its optimum performance at different pH values: nearly pH independent for the Fenton process [Pignatello, J.J. (1992)], optimum at pH 2.8 for the Fenton-like reaction [Pignatello, J.J. (1992)], and clearly pH dependent for photo-Fenton reaction [Pignatello, J.J., et al. (1999)]. Data concerning TOC degradation of paper mill effluents at several pH showed that the faster removal of TOC takes place at pH=2.8 [Pérez, M., et al. (Submit.)]. A very acid media or a neutral-basic media slows down the process. The low activity detected for high pH values can be explained by the formation and precipitation of $\text{Fe}(\text{OH})_3$, a process that hamper the development of photo-Fenton and Fenton-like reactions. The decrease of activity for pH values below the optimum is understandable taking into account that Fe (III) forms different complex species in solution, and the quantum yield of light absorption by Fe(III) is directly depending on the specific specie responsible for the absorption. Table 2 shows the predominant iron species at different pH ranges [Safarzadeh-Amiri, A., et al. (1996)].

Table 1. *Compounds found by GC-MS in the textile effluent after hydrolysis.*

<i>Compound</i>	<i>Retention time</i>	<i>Reliability</i>
Aromatic compounds		
benzoic acid	10.80	97 %
benzeneacetic acid	12.90	76 %
3-methyl benzoic acid	13.72	94 %
ethyl ester 4-ethoxy- benzoic acid	19.32	96 %
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	24.70	98 %
Linear acids		
nonanoic acid	13.60	95 %
decanoic acid	16.27	96 %
undecanoic acid	19.13	96 %
dodecanoic acid	20.70	99 %
tetradecanoic acid	24.80	98 %
pentadecanoic acid	26.80	97 %
hexadecanoic acid	29.10	99 %
heptadecanoic acid	30.76	96 %
octadecanoic acid	32.62	93 %
Other compounds		
2,2'-oxybis-ethanol	5.30	83 %
decane	5.48	91 %
2,8-dimethyl-4-methylene-nonane	7.73	86 %
2-decanone	10.71	90 %
methyl ester nonaic acid	17.80	70 %
2-butyl octanoic acid	19.30	91 %
2-propylnonanoic acid	19.35	72 %
2-methyl undecanoic acid	19.72	91 %

Table 2. Hydrated Fe(III) species in solution and the range of pH where they are predominant.

<i>Fe specie</i>	<i>pH</i>
Fe (H ₂ O) ₆ ³⁺	1-2
Fe (OH)(H ₂ O) ₅ ²⁺	2-3
Fe (OH) ₂ (H ₂ O) ₄ ⁺	3-4

The main species at pH 2-3, Fe (OH)²⁺(H₂O)₅, is the one with the largest light absorption coefficient and quantum yield for OH[•] production in the range 280-370 nm [Benkelberg, H-J. and Warneck, P. (1995)]. Thus, it is also the species that potentially regenerates more Fe(II). At lower pH, where Fe³⁺(H₂O)₆ is more concentrated, the effectiveness of light absorption, regeneration of Fe(II) and, eventually, TOC degradation is lower. For larger pH Fe(OH)₂⁺(H₂O)₄ dominates, but the solution becomes unstable with Fe(OH)₃ precipitation [Benkelberg, H-J. and Warneck, P. (1995)]. On the other hand, the pH during the reactions always evolved toward the optimal pH value (approximately 3) [Pérez, M., et al. (Submit.)]. Thus, pH 3 was the pH used in all the experiments presented in this study.

Blank experiments were carried out in order to ascertain whether Fenton, Fenton-like and Photo-Fenton reactions take place with such an organic content. When 100 mL of the effluent were mixed with 100 ppm of Fe (II) under Xe lamp irradiation and at 40°C, no TOC removal took place. The same behavior was observed when 1000 ppm of H₂O₂ were mixed with the effluent in absence of Fe (II), shown in figure 1. In contrast, the presence of both H₂O₂ and Fe (II) at 40 °C and under light irradiation produced a TOC reduction of 150 ppm (24%) after 30 minutes, and longer reaction times involved larger reductions. Clearly, Fenton reagent under irradiation improves TOC removal. Light can play two different roles that would lead to an improvement of the reaction yields: a) it drives photo-Fenton reaction, producing additional hydroxyl radicals and the recovery of Fe(II) needed in Fenton reaction. The photo-Fenton reaction may involve direct photolysis of ferric ion (equation 5) or photolysis of Fe(III)-peroxy complexes [Pignatello, J.J., et al. (1999)]. b) it can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe(III) and organic compounds, a process that has been well proven for the complexes formed between Fe(III) and the carboxylic acid moiety [Hislop, K.A. and Bolton, J.R. (1999)]. Large quantities of carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate.

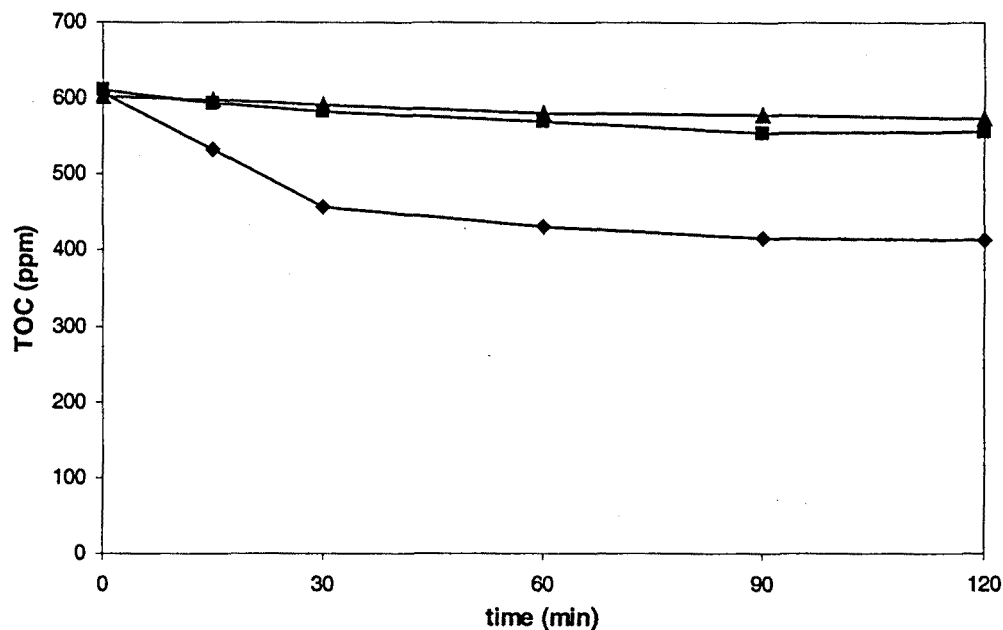


Figure 1. TOC of the textile effluent vs. reaction time for several experimental conditions: 100 ppm of Fe(II) (■); 1000 ppm of H₂O₂ (▲); 1000 ppm of H₂O₂ and 100 ppm of Fe(II), (◆). pH=3, T=40 °C, xenón irradiation.

The beneficial effect of temperature was carefully tested in a set of experiments where three different temperatures (25, 40 and 70 °C) were used in the dark and under irradiation of the Xe lamp. The decrease of organic concentration with time due to oxidative degradation of the textile bleach effluents by Fenton and Photo-Fenton reactions at these three different temperatures is shown in Figure 2.

From the differences between the pairs of experiments carried out under the same conditions (irradiation or absence of light) and different temperature it is clear that temperature markedly influences the degree of TOC removal.

As can be seen in Figure 2, no important differences exist during the first minutes of reaction if the process is carried out in presence or absence of light. This can be explained by taking into account two facts: a) the initial TOC decrease is mainly due to the dark Fenton reaction, which is faster than Fenton-like [Pignatello, J.J. (1992)] or photo-Fenton reactions [Sun, Y. and Pignatello, J.J. (1993)]. b) Fe (II) is clearly the limiting reagent and as long as Fe(II) is available the same initial reaction rate is expected.

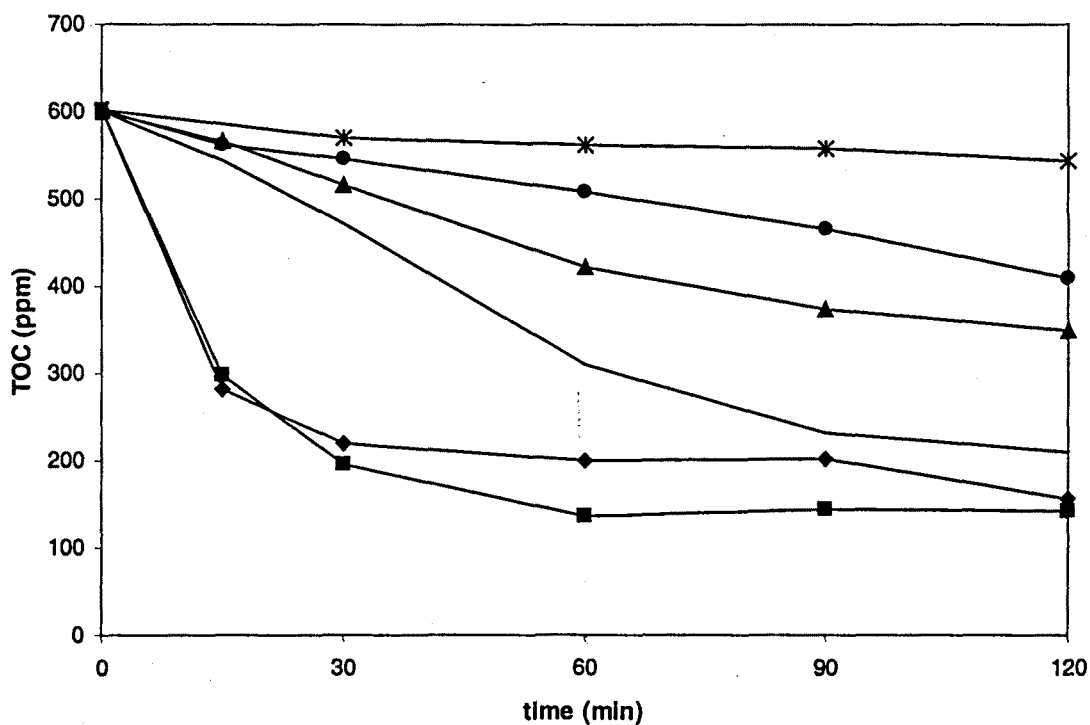


Figure 2. Effect of temperature on TOC removal. 25 °C in the dark (*); 25 °C under Xe lamp irradiation (●); 40 °C in the dark (▲); 40 °C under Xe lamp irradiation (—); 70 °C in the dark (◆); 70 °C under Xe lamp irradiation (■). $[H_2O_2]_0=10000$ ppm, $[Fe(II)]_0=100$ ppm, pH=3.

Under the experimental conditions tested here, Fe(II) consumption takes place in few seconds, producing the majority of TOC decrease observed after 15 minutes of reaction (when the first samples were taken). Thus, for these short reaction times no effect is observed due to the presence of light.

Dark reaction rates after Fe(II) consumption are controlled by the Fenton-like process between H_2O_2 and the Fe(III) formed in the first seconds of direct Fenton reaction. The Fenton-like process regenerates Fe(II) (see reactions 2-4) which, in presence of excess H_2O_2 is readily transformed giving Fe(III). Thus, an effective iron cycling takes place, with approximately constant Fe(III) concentration, traces of Fe(II), and a fairly constant oxidant intermediate production.

When the experiment was carried out at 70°C, levels of TOC removal over 65% were attained after just 30 minutes of reaction, both, in the dark and under irradiation. Since the 100 ppm of Fe(II) cannot directly produce enough $OH\cdot$ radicals through the Fenton reaction to account for the total level of TOC removal, the acceleration of Fenton reaction with temperature cannot be the only cause of such an observation. The

temperature seems to be assisting alternative ways of H_2O_2 cleavage and $OH\cdot$ formation, or Fe(II) recovery. The photo-Fenton reactions has not an important role, and the recovery of Fe(II) from Fe (III) seems to be taking place more effectively through the Fenton-like reactions (equations 2-4). Blanks experiments showed that neither the irradiation nor the temperature alone can produce noticeable decreases of TOC, the simultaneous presence of Fe(II) and H_2O_2 being always necessary. On the other hand, in the experiments carried out at 25 and 40°C, the levels of TOC removal increase under light irradiation, making clear the important role of the light driven reactions. A similar behavior has been observed during the treatment of bleaching Kraft mill effluents with Fenton and photo-Fenton systems [Pérez, M., et al. (Submit.)].

In any case, temperature is a key parameter that has to be taken into account, specially for those applications where TOC removal rate can be increased by using low cost heat (heat exchangers, co-generation, etc.). It is important to remark that in comparison to most industrial wastewaters, the temperature of textile effluents is unusually high. During the dyeing process, rinse waters temperatures up to 90 °C are normally encountered [Lin, S.H. and Peng, C.F. (1994)].

Although the Fenton reaction has been widely studied, there is still not an agreement on the ratio $[H_2O_2]/[Fe(II)]$ that gives the best results. Many authors have reported the use of different ratios of the two reactants, as can be seen on table 3.

Table 3. Ratios $[H_2O_2]/[Fe(II)]$ used in the works of different research groups.

	<i>Ratio Fenton Reagents</i>		<i>Referencia</i>
Molar ratios	3:1:1	$H_2O_2/Fe(II)/Phenol$	Eisenhauer, 1964
	1:4:20	$H_2O_2/Fe(II)/Chlorobiphenyls$	Sedlak et al., 1991
	100:1:16	$H_2O_2/Fe(II)/Clorophenols$	Barbeni et al., 1987
	11:1	$H_2O_2/Fe(II)$ for 2,4-Dichlorofenol	Tang et al., 1996
	40:1:4	$H_2O_2/Fe(II)/4-Chlorofenol$	Ruppert et al., 1993
	400:1	$H_2O_2/Fe(II)$ treating real wastewater.	Bauer et al., 1997
ppm ratios	50:1	$H_2O_2/Fe(II)$	Esplugas et al., 2001
	100:1:50	$H_2O_2 / Fe(II)/$ real wastewater	Pérez et al. Submit.

Large excess of H_2O_2 or Fe^{2+} might be detrimental, since these species can react with some of the intermediates like $OH\cdot$, responsible of the direct oxidation of the organic load:



precluding the extent of mineralization. Thus, in order to check the effect that different reagent ratios have on the reactions, experiments with several ratios of $H_2O_2/Fe(II)$ were also conducted.

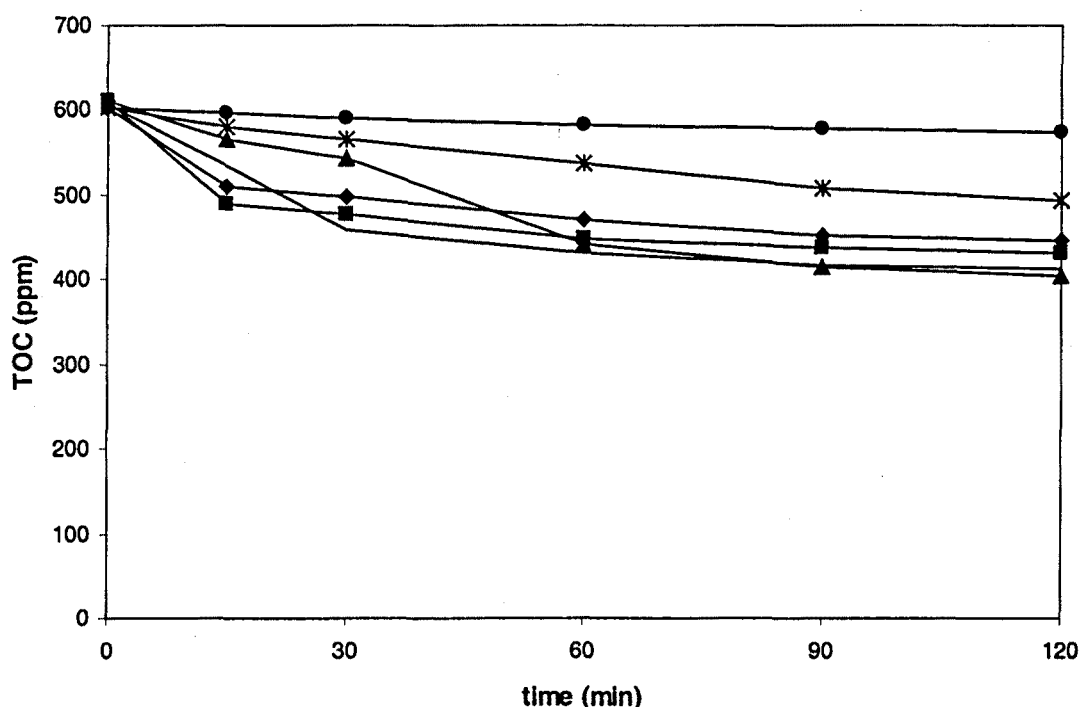


Figure 3. Effect of $Fe(II)$ doses on TOC reduction. The initial concentrations of $Fe(II)$ were as follows: 0 ppm (●); 25 ppm (*); 50 ppm (▲); 100 ppm (—); 200 ppm (■); 400 ppm (◆). $[H_2O_2]_0 = 1000$ ppm, $pH = 3$, $T = 40$ °C, Xe lamp irradiation.

Figure 3 shows that, in general, increasing initial quantities of iron in solution produce increasing rates of degradation. Although during the first minutes the reaction with more $Fe(II)$ proceeds at a faster rate, at long reaction times the experiment with 200 and 400 ppm of $Fe(II)$ produces a TOC decay that is slightly minor than the one obtained with 100 ppm. This change on behavior with time can be explained by taking into account that Fenton reaction, which is completed after few seconds, benefits from a larger $Fe(II)$ load, while detrimental reactions like 6 and 7, due to the low concentration

of OH^\bullet , need more time to manifest, and their effects only appear for long enough reaction times, when they compete with slower reactions as Fenton-like, photo-Fenton, photochemical processes, etc.

As can be seen for 1000 ppm H_2O_2 , 50 and 100 ppm of Fe(II) seem to be the more suitable doses for long reaction time. 5:1 and 10:4 $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratios show the faster rate of TOC degradation during the first minutes. This is in agreement with the fact that Fenton reaction dominates the first minutes of the process and a larger concentration of reactants directly increases the reaction rate. With a 20:1 $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio there is a clear reduction in the initial amount of Fe(II) used, and the role played by Photo-Fenton and Fenton-like reactions is more important. On the other hand, the use of large quantities of Fe in solution has a negative effect from the applied point of view, since it implies the need of an additional treatment step for Fe removal.

Figure 4 contains data concerning experiments with several initial H_2O_2 doses. In this case it is clear that increasing amounts of H_2O_2 lead to larger TOC removal, with no detrimental effects detected for the highest H_2O_2 . Nevertheless, the small difference between the TOC removal attained with 2500, 5000 and 10000 ppm of H_2O_2 indicates that improvements of reaction rate may not compensate the large amounts of oxidant consumed.

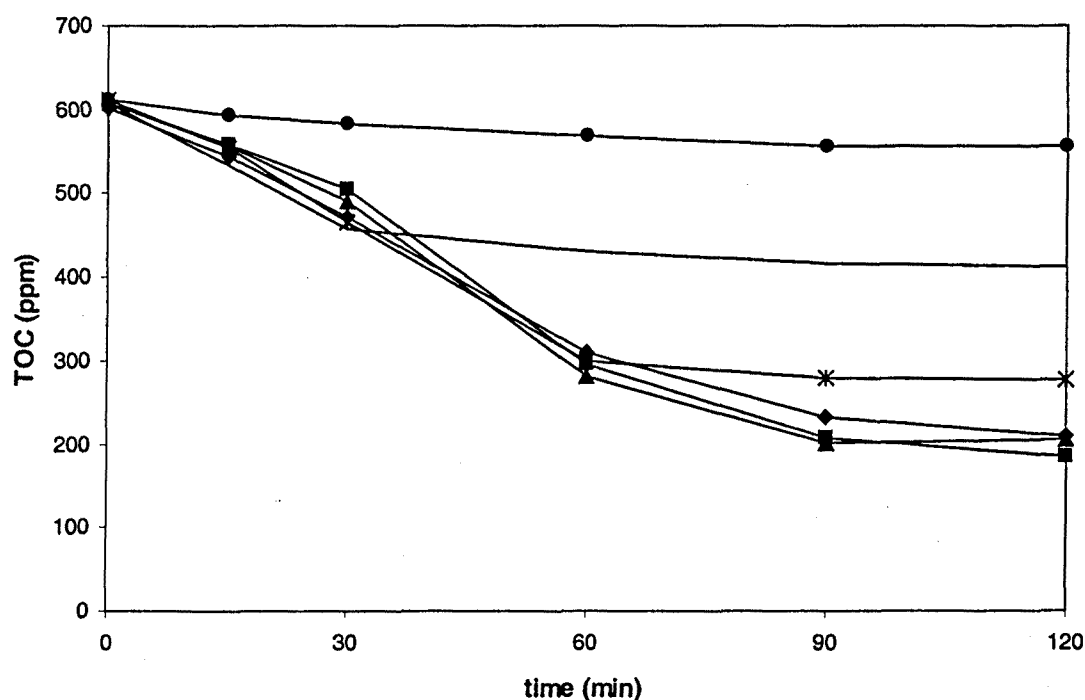


Figure 4. Effect of H_2O_2 doses on TOC reduction. The initial concentrations of H_2O_2 were as follows: 10000 ppm (◆); 5000 ppm (■); 2500 ppm (▲); 1500 ppm (*); 1000 ppm (—); 0 ppm (●). $[\text{Fe(II)}]_0 = 100$ ppm, $\text{pH} = 3$, $T = 40$ °C, Xe lamp irradiation.

In all these cases 50% TOC reduction after 1 hour of reaction and around 70% after 2 hours of reaction were obtained. It is interesting to note that, for the least H_2O_2 concentrated experiments the TOC removal slows down to few ppm per hour, showing that, even for Fenton-photo-Fenton systems large enough concentrations of H_2O_2 are essential.

The intensity and the wavelengths emitted by the light source are key conditions when trying to describe the participation of the light driven reaction. It is specially interesting, from the application point of view, the possibility of using solar light. Figure 5 shows the differences in TOC removal when three different light sources are used. A 10:1 concentration ratio (1000ppm of H_2O_2 , per 100 ppm Fe (II)) was used in all experiments.

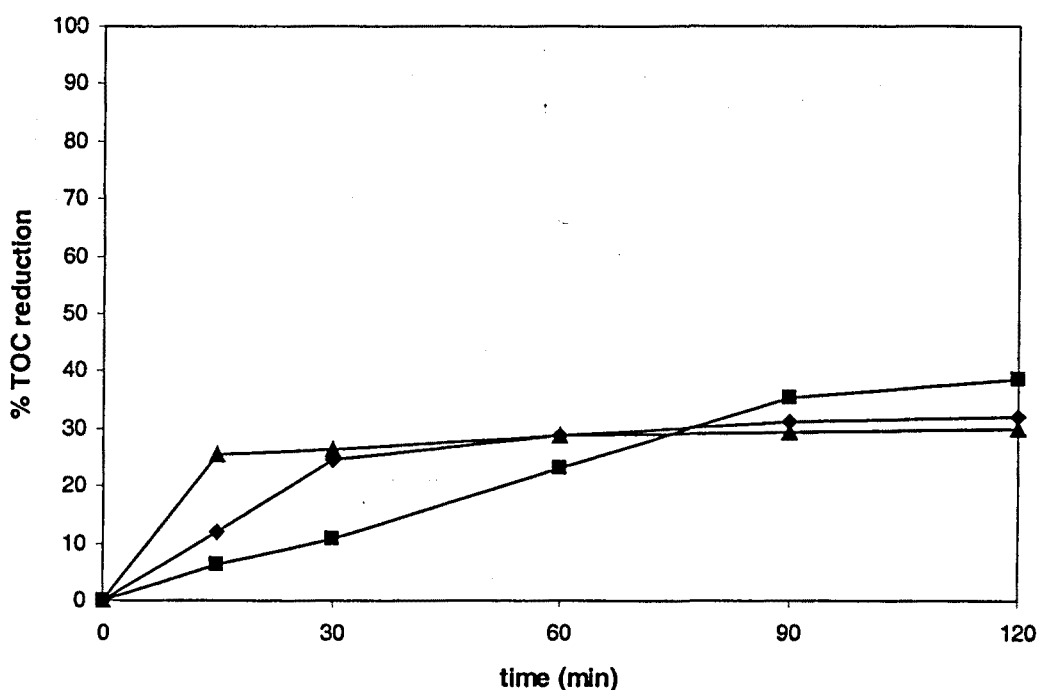


Figure 5. TOC decay vs. reaction time when using different light sources. UVA light (■); solar light (▲); Xe light (◆). $[\text{H}_2\text{O}_2]_0=1000$ ppm, $[\text{Fe(II)}]_0=100$ ppm, $\text{pH}=3$ $T^\circ=40^\circ\text{C}$.

An assessment of the energy input entering the reactor gave: $3.833 \cdot 10^{-5} \text{ W cm}^{-2}$ (below 500 nm) for the UVA lamp; $1.653 \cdot 10^{-3} \text{ W cm}^{-2}$ (below 500 nm) for the Xenon light, and $5 \cdot 10^{-3} \text{ W cm}^{-2}$ (below 400 nm, with a presumably larger photon input below 500 nm) for the solar light. The behavior of the system during the first hour obeys this order of energies, with the solar irradiation being the most efficient light source. However, at long enough reaction time there is a trend change and UVA light gives the larger ratio of TOC removal. It is difficult to find an explanation for such a behavior but it seems

that a intense irradiation favors the fast exhaustion of H_2O_2 through non efficient reactions while mild irradiation consumes less oxidant in parallel and undesired photochemical reactions. Difficulties on maintaining the solar irradiation at a constant temperature could also be taken into account when trying to find an explanation for such an unexpected behavior.

Conclusions

The degradation of the organic content of a textile bleaching effluent has been successfully carried out by the simultaneous use of Fenton reagent and UVA irradiation. From the data is it clear that, under the specific experimental conditions of the work Fenton reaction applies during the very first seconds, while photo-Fenton and Fenton-like reactions are only important after several minutes. Irradiations were done with different light sources, being more effective for long irradiation those with lower photon output. Solar light irradiation was found to be highly effective, opening the possibility of extended low cost applications. Temperature is a key parameter, markedly increasing reaction rates. Initial concentrations of Fe(II) in solution above 100 ppm were found not to improve the rate of the reaction, while up to the values tested in this work the reactivity was larger the higher the concentration of H_2O_2 .

The mineralization of textile bleaching effluents with simultaneous use of Fenton, Fenton-like and photo-Fenton reactions has clear applied advantages, advantages that are outlined through the text.

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References

- Barbeni, M., Minero, C., Pelizzetti, E., Borgarello, E. and Serpone, N. (1987) Chemical degradation of chlorophenols with Fenton's reagent. *Chemosphere*. **16**, 2225-2237.
- Bauer, R. and Fallmann, H. (1997) The photo-Fenton oxidation – a cheap and efficient wastewater treatment method. *Res.Chem.Intermed.* **23**, 341-354.
- Benkelberg, H-J. and Warneck, P. (1995) Photodecomposition of iron (III) hydroxo and sulfato complexes in aqueous solution: wavelength dependence of OH and SO₄⁻ quantum yields. *J. Phys. Chem.* **99**, 5214-5221.
- Bossmann, S.H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E.P., Payawan, L., Straub, M., Wörner, M., Braun, A.M. (1998) New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. *J. Phys. Chem.* **102**, 5542-5550.
- Canadian Pulp and Paper Association Standard Method H.5 – *Color of Pulp Mill Effluents* (Approved method, December 1991; Revised, August 1993).
- Chamarro, E., Marco, A. and Esplugas, S. (2001) Use of Fenton reagent to improve the biodegradability of effluents. *Wat. Res.* **35**, 1995-1999.
- Dorica, J. (1992) Removal of AOX from bleach plant effluents by alkaline hydrolysis. *J. Pulp Paper Sci.* **18**, 231-237.
- Eisenhauer, H.R. (1964) Oxidation of phenolic wastes. *J. Water Pollution Control Federatio.* **36**, 1116-1128.
- Hislop, K.A. and Bolton, J.R. (1999) The photochemical generation of hydroxyl radicals in the UV-vis/Ferrioxalate/H₂O₂ system. *Environ. Sci. Technol.* **33**, 3119-3126.
- Hoffmann, M.R., Martin S.T., Choi, W. and Bahnemann, D.W. (1995) Environmental applications of semiconductor photocatalysis. *Chem.Rev.* **95**, 69-96.
- Kiwi, J., Pulgarin, C. and Peringer, P. (1994) Effect of Fenton and photo-Fenton reactions on the degradation and biodegradability of 2 and 4-nitrophenols in water treatment. *Appl. Catal. B: Environm.* **3**, 335-350.

- Klare, M., Waldner, G., Bauer, R., Jacobs, H. and Broekaert, J.A.C. (1999) Degradation of nitrogen containing compounds by combined photocatalysis and ozonation. *Chemosphere*, **38**, 2013-2025.
- Lin, S.H. and Peng, C.F. (1994) Treatment of textile wastewater by electrochemical method. *Wat. Res.*, **28**, 277-282.
- Linsebigler, A.L., Lu, G. and Yates, J.T. (1995) Photocatalysis on TiO₂ surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **95**, 735-758.
- Logager, T., Holcman, J., Sehested, K. and Pedersen. (1992) Oxidation of ferrous ions in acidic solutions. *Inorg. Chem.*, **31**, 3523-3529.
- Mills, A. and Le Hunte, S. (1997) An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A: Chem.* **108**, 1-35.
- Muller, T.S., Sun, Z., Kumar, G., Itoh, K. and Murabayashi, M. (1998) The combination of photocatalysis and ozonolysis as a new approach for cleaning 2,4-dichlorophenoxyacetic acid polluted water. *Chemosphere*. **36**, 2043-2055.
- Pérez, M., Torrades, F., García Hortal, J.A., Domènech, X. and Peral, J. (1997) Removal of organic contaminants in paper pulp treatment effluents by TiO₂ photocatalyzed oxidation. *J. Photochem. Photobiol. A: Chem.* **109**, 281-286.
- Pérez, M., Torrades, F., Garcia-Hortal, J.A., Domènech, X. and Peral, J. Removal of organic contaminants in paper pulp treatment effluents by Fenton and photo-Fenton reactions. Submitted to *Appl. Catal. B: Environm.*
- Peyton, G.R. (1990) Oxidative treatment methods for removal of organic compounds from drinking water supplies, in *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, Lewis Publishers, Chelsea. 313-362.
- Pignatello, J.J. (1992) Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* **26**, 944-951.
- Pignatello, J.J., Liu, D. and Huston, P. (1999) Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environ. Sci. Technol.* **33**, 1832-1839.
- Ruppert, G., Bauer, R. and Heisler, G. (1993) The photo-Fenton reaction – and effective photochemical wastewater treatment process. *J. Photochem. Photobiol. A: Chem.* **73**, 75-78.

Safarzadeh-Amiri, A., Bolton, J.R. and Cater, S.R. (1996) The use of iron in advanced oxidation processes. *J. Advan. Oxid. Technol.* **1**, 18-26.

Sánchez, L., Peral, J. and Domènech, X. (1998) Aniline degradation by combined photocatalysis and ozonation. *App. Catal. B: Environm.* **19**, 59-65.

Sedlak, D.L. and Andren, A.W. (1991) Oxidation of chlorobenzene with Fenton's reagent. *Environ. Sci. Technol.* **25**, 777-782.

Sun, Y. and Pignatello, J.J. (1993) Photochemical reactions involved in the total mineralization of 2,4-D by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$. *Environ. Sci. Technol.* **27**, 304-310.

Tanaka, K., Abe, K. and Hisanaga, T. (1996) Photocatalytic water treatment on immobilized TiO_2 combined with ozonation. *J. Photochem. Photobiol. A: Chem.* **101**, 85-87.

Tang, W.Z. and Huang, C.P. (1996) 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environ. Technol.* **17**, 1371-1378.

Torrades, F., Peral, J., Pérez, M., Domènech, X., Garcia Hortal, J.A. and Riva, M.C. (2001) Application of heterogeneous photocatalysis and ozone to destruction of organic contaminants in bleaching kraft mill effluents. *Tappi J.* **84** (6), 63-72.

Tzitzzi, M., Vayenas, D.V. and Lyberatos, G. (1994) Pretreatment of textile industry wastewaters with ozone. *Wat. Sci. Tech.* **29**, 151-160.

7. CONCLUSIONS

The use of Advanced Oxidation Processes (AOPs), including Photochemistry, Photocatalysis, Ozonation, Fenton, Fenton-like and Photo-Fenton reactions, for the purpose of decreasing the levels of pulp and textile bleaching wastewater contamination, has led to the following conclusions:

1. Direct photolysis, specially in presence of Fe^{2+} , is less cost effective than photocatalysis. The observed differences in the color of wastewaters during treatment point toward differences in reaction mechanisms and intermediates formed, between the two techniques.
2. The kinetics of TOC removal during Photocatalytic treatment of generated bleaching pulp effluents, after the first adsorption stage, follows a zero order equation. This behavior is best explained as a particular case of the more general Langmuir-Hinselwood equation.
3. No evidences of Fe^{2+} supported photocatalysis are found, and the TOC decrease produced in the systems containing TiO_2 , Fe^{2+} and H_2O_2 seems the consequence of photocatalysis and Fenton, Fenton-like and Photo-Fenton reactions working in parallel.
4. The light intensity reaching the reaction vessel has an effect on the reaction rate. The TiO_2 catalyst, under 6W of low power UVA radiation, is a lower cost treatment with an associated slow rate of TOC reduction. The use of high power light (125 W) increased the reduction rate of parameters of higher environmental impact, i.e., AOX, TOC and total phenols. The toxicity of the wastewater was significantly reduced in the first stages of the reaction.
5. Photocatalysis treatment using high power light (125 W), as shown by GC-MS analysis, is efficient in the elimination of chlorophenolic compounds in the bleaching pulp mill effluent.
6. The experimental design was a valuable tool in studying the role that the studied variables played in the photocatalysis of cellulose bleaching effluent. The most significant effect was ascribed to pH and TiO_2 load.
7. Addition of H_2O_2 to the photocatalytic reaction led to a minor improvement in TOC and AOX reduction, at least in the ranges we studied; that is not justified considering the increased costs incurred. However, because it is a first-order interaction with the catalyst, it enhances the COD removal.

8. Mesoporous, photocatalytic TiO₂ films can be securely attached to acrylic sheets and act as waveguides. These waveguides can be incorporated into photoreactor designs to dramatically increase the amount of catalyst that can be illuminated with a single light source. They are suitable to be used to photocatalytically oxidize organic compounds.
9. A synergistic effect by simultaneously applying both photocatalysis and ozonation treatments to the generated bleaching pulp effluent was observed. On the other hand, even an ozonation pretreatment followed by a photocatalysis step on industrial bleaching pulp effluent leads to TOC reduction rates that are comparable to separated treatment techniques, 50 % cost reduction is achieved related to the ozonation process after only three hours treatment.
10. Ozone treatment significantly removes a large amount of TOC, especially under UVA light irradiation. Moreover, the use of light during ozonation produces a noticeable decrease in treatment cost.
11. The presence of iron ions in solution when an ozone/UVA treatment is carried out in a bleaching mill wastewater not only generates high rates of TOC removal (90%), it also results in a significant cost reduction (15%). Iron ions support the effect of ozonation by generating hydrogen peroxide. The presence of both Fenton reagents in the system leads to Fenton, Fenton-like and Photo-Fenton reactions.
12. Sequential processing (stirred iron with or without light irradiation, followed by an ozonation stage) led to a reduction in the cost of treatment of up to 50 % and with a level of TOC removal comparable to the ozone/UVA process. Iron load did not have a noticeable effect on cost reduction. Similar conclusions were obtained on the synthetic sample of 2,4-dichlorophenol, where we found a 70 % reduction in cost by using the sequential treatment. At the same time the amount of TOC and COD removed was 90 % and 95 % respectively.
13. Degradation of the organic contents of bleaching Kraft mill and textile mill effluents have been successfully carried out by simultaneously applying Fenton reagents under suitable light irradiation. pH = 3 is the optimal value for the simultaneous occurrence of all reactions.
14. Solar light is an efficient and economical source of irradiation. The use of this natural source of energy, in presence of the Fenton reagent, reduced the total cost of two hour treatment up to 70 %
15. Careful experimental design was invaluable in determining the right Fenton reagent ratio and the effect of temperature in the Fenton complex mechanism.

16. Non optimal, initial concentrations of Fenton reagent were found to be detrimental due to competitive reactions of this reagent with the oxidative species. Initial concentrations of Fe(II) in solution, above a certain level which depends on the contaminant load, were found to be detrimental. However, we found the reactivity with the values of Fe(II) used in this work was larger as higher the concentration of H₂O₂.
17. We found temperature to be a key parameter. The temperature could markedly increase the reaction rates, even without light irradiation, of a Fenton reaction. Temperature seems to be particularly significant in increasing TOC removal when the system is under a low reagent load or the reagent ratios are inadequate. In particular, temperature becomes a key parameter when the use of high levels of iron ions on the treated wastewaters are prohibited or when it is desirable to reduce reagent costs. A decrease in cost of around 80% is possible by just increasing the temperature from 25°C to 40°C.
18. The bubbling of O₂ through the solutions does not improve the reaction yields. This suggests that, under the specified conditions, O₂ saturation occurs.
19. Fenton, Fenton-like and Photo-Fenton reactions are efficient, as shown by GC-MS analysis, in the elimination of chlorophenolic compounds from chlorine bleaching effluents.

