

Coupled photo-Fenton–biological system: effect of the Fenton parameters such as residual H_2O_2 , Fe^{2+} and pH on the efficiency of biological process

Rosa Mosteo, Damien Gummy and Cesar Pulgarin

ABSTRACT

The aim of this research work is to evaluate the performance of packed-bed bioreactors under typical conditions of photo-Fenton treatment (residual iron, residual hydrogen peroxide, acidic pH). The target pollutant selected was 4-Chlorophenol which is included in the list of Priority Substances (Decision No 2455/2001/EC) in the field of water policy and amending Directive 2000/60/EC. It was found that the biological process operated correctly during eight days when the pH was in the range of 3.5–7. In the same way, the presence of hydrogen peroxide in similar concentrations to that used in the photo-Fenton process was not negative on the biological activity. On the other hand, the presence of residual iron in the biological treatment could not be observed as a consequence of the optimal dosage used for the photo-Fenton treatment. The iron dosage is still low enough to ensure non-inhibitory effects. The results obtained in this study can provide a practical knowledge for a real application.

Key words | integrated chemical and biological process, photo-Fenton process, wastewater treatment

Rosa Mosteo

Departamento de Ingeniería Química y Tecnologías del Medio Ambiente, Universidad de Zaragoza, España, Spain
E-mail: mosteo@unizar.es

Damien Gummy

Cesar Pulgarin

Groupe de Génie Electrochimique, Institut des sciences et ingénierie chimique, Ecole Polytechnique Fédérale de Lausanne, EPFL, CH-1015 Lausanne, Suisse, Switzerland
E-mail: cesar.pulgarin@epfl.ch

INTRODUCTION

Chlorophenols have been used as preservative agents for wood, paints, vegetable fibres and leather and as disinfectants. In addition, they have been widely employed in many industrial processes as synthesis intermediates or as raw materials in the manufacturing of herbicides, fungicides, pesticides, insecticides, pharmaceuticals and dyes (Pera-Titus *et al.* 2004).

These substances constitute a particular group of priority toxic pollutants listed by the European Decision 2455/2001/EC and by the US Environmental Protection Agency in the Clean Water Act (Keith & Telliard 1979; Hayward 1998). Although many chlorophenols are biodegradable under aerobic or anaerobic conditions they are rather toxic to microorganisms. For instance, 20–30 mg L⁻¹ of 4-chlorophenol can strongly inhibit activated sludge bacteria (Ren & Frymier 2002).

Advanced Oxidation Processes (AOPs) are based on the in-situ generation of highly potent chemical oxidants such as the hydroxyl radical (OH[•]), a powerful non-selective chemical oxidant, which has a strong oxidation potential and acts very rapidly with most organic compounds. They are very promising methods for the remediation of wastewaters containing non-biodegradable pollutants (Pulgarin & Kiwi 1996; Herrera *et al.* 1998; Sarria *et al.* 2002).

Many systems are classified under this wide definition of AOPs. Among them, Fenton, photo-Fenton, photocatalysis, ozonation and wet oxidation can be mentioned. Most of the AOPs use a combination of strong oxidants, e.g. O₃ and H₂O₂, with catalysts, e.g. transition metals ions or photocatalysis, and irradiation, e.g. ultraviolet or visible. Fenton process involves the reaction of ferrous ions (catalyst) and hydrogen peroxide (oxidizing agent) to form

the active hydroxyl radicals (Fenton process). The Fenton reaction is markedly accelerated by light so the photo-Fenton reaction typically gives faster rates and a higher degree of mineralization (Pignatello *et al.* 2006). Furthermore, photo-Fenton reaction can be driven with low energy photons in the visible part of the spectrum. Thus, photo-Fenton processes are potential low cost AOPs that can be achieved under solar irradiation (Ormad *et al.* 2006).

On the other hand, the use of AOPs as a pre-treatment step to enhance the biodegradability of wastewaters containing recalcitrant or inhibitory pollutants can be justified if the resulting intermediates are easily degradable by microorganisms in further biological treatment (Oller *et al.* 2007). Unfortunately, photochemical pre-treatments can also produce more toxic and/or non-biodegradable photoproducts which can even inhibit the subsequent biological stage (Essam *et al.* 2006). These processes should be therefore be carefully investigated and optimized to minimize the duration of the physicochemical step while ensuring proper conditions for subsequent biological treatment.

The first coupled flow system was developed in our laboratory using photo-Fenton reaction as pretreatment (Bandara *et al.* 1997; Pulgarin *et al.* 1999; Parra *et al.* 2000; Sarria *et al.* 2003). Simple biodegradability and ecotoxicity test can fail to predict accurately whether process coupling would be effective. This is particularly true for toxicity test as in several cases chemical oxidation may lead to increase toxicity being accompanied by increased biodegradability. Many papers have yet related the feasibility of the coupling, using the Zahn-Wellens procedure to assess the biocompatibility of the photo-treated solutions (Lapertot *et al.* 2007). In this study the photo-degraded solutions was more precisely investigated using packed-bed bioreactors.

It has been demonstrated that immobilized microbial systems greatly improve bioreactor efficiency; for instance, increasing process stability and tolerance to shock loadings, allowing higher treatment capacity per biomass unit and generating relatively less biological sludge (Lewandowski & DeFilippi 1998).

The paper reports the results of coupled photo-Fenton–biological treatment system applied to remove the 4-Chlorophenol presents in aqueous solutions. The main objective of this study is to evaluate the performance of the

biological treatment under typical conditions of photo-Fenton treatment (residual Fe, H₂O₂, acidic pH). Results can provide a practical knowledge for a real application.

MATERIALS AND METHODS

Chemicals

The target solution consists of a 100 mg L⁻¹ (0.78 mM) 4-Chlorophenol (4-CP), which is obtained from Acros Organics. Table 1 summarizes the main features of this compound for the concentration used in this study.

Ferrous iron sulfate (FeSO₄·7H₂O), hydrogen peroxide (30%, w/v) are obtained from Flucka. Sulphuric acid and sodium hydroxide used for pH adjustment are reagent grade.

Analytical determination

Mineralization is followed by measuring the Total Organic Carbon (TOC) by direct injection of filtered samples into a Shimadzu-5050A TOC analyser provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. 4-Chlorophenol concentration and its intermediates of degradation are analyzed using reverse-phase liquid chromatography (flow 1 ml min⁻¹) with UV detector in a HPLC-UV with a Spherisorb C18 column (4.6 mm–250 mm, from Macherey–Nagel) and a guard column (Macherey–Nagel 4.6 mm–10 mm). The mobile phase is a mixture of acetonitrile/water, and a gradient evolution from 5% to 80% of acetonitrile is used. Ultra pure distilled–deionised water obtained from a Milli-Q (Millipore Co.) system and HPLC-grade organic solvents are used to prepare all the solutions. H₂O₂ concentration is determined with Merck peroxide test strips (O₂²⁻) (0 to 25 mg L⁻¹). Chemical Oxygen Demand (COD) is determined with Hach COD test kits (0–150 mg O₂ L⁻¹). Biochemical Oxygen Demand (BOD₅) is measured during 5 days using an Hg free WTW 2000 Oxitop© unit

Table 1 | Main features of 4-chlorophenol aqueous solution

4-CP concentration	TOC	COD	BOD ₅	COD/TOC
100 mg L ⁻¹	56 mgC L ⁻¹	157 mgO ₂ L ⁻¹	0 mgO ₂ L ⁻¹	2.80

thermostated at 20°C. Experiments are carried out according to method 5210D of *Standard Methods* (Cleresci *et al.* 2005). The activated sludge obtained from a secondary effluent of the activated sludge treatment plant of Morges (Switzerland) is used as inoculum.

Experimental set-up

Photo-Fenton experiments

The Photo-Fenton experiments are performed using 1 L Pyrex flask with a cut-off at $\lambda = 290$ nm placed into Hanau Suntest Simulator. The radiation source employed is a xenon lamp and the total radiant flux (100 mWcm^{-2}) was measured with an YSI Corporation powermeter. The lamp has a λ distribution with about 0.5% between 300 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum (Yuranova *et al.* 2006).

At the beginning of the experiments, while reactors are kept in the dark, a solution of 4-chlorophenol is added to the reactor at a concentration of 100 mgL^{-1} (0.78 mM). Then, the pH is adjusted to 2.8, which has been indicated previously as optimal pH (Bacardit *et al.* 2007), and Fe^{2+} is added to the reactors at a concentration of 20 mgL^{-1} (0.36 mM). Finally, H_2O_2 is added at different concentrations to the reactors (2.33 M, 2.90 M, 4.65 M) in order to know the best concentration for this reactive, and the solar lamp is turned on. The aqueous pollutant solutions are magnetically stirred throughout irradiation, opened to air. The disappearance of 4-CP is monitored by HPLC after filtration with millipore filters ($0.45 \mu\text{m}$). The solution is irradiated until the total disappearance of H_2O_2 (controlled with Merck peroxide test strips).

All photo-Fenton experiments are performed by duplicate. In order to consider possible interferences, a control experiment is also performed without the addition of hydrogen peroxide and iron salts to quantify possible losses of organic matter by volatilisation.

Biotreatment experiments

As illustrated in Figure 1 and Figure 2, four aerated packed-bed immobilised biomass reactors are operated in parallel. Each bioreactor consisted of a 0.24 L glass column containing *ca.* 0.6 L packing plastic ring supports colonized by



Figure 1 | Picture of the Pyrex glass reactor filled with polyethylene rings employed for Biodegradation experiments.

activated sludge from the wastewater treatment plant of Morges (Switzerland). Liquid in the columns is circulated with peristaltic pumps. This experimental setup was previously described in details in our precedent work (Lapertot *et al.* 2007). In order to homogenize the bacterial population throughout each column and between all of them (in fact, four biofilters are run simultaneously), wastewater from the primary decanter was recirculated inside the biofilter from upside down during a few days until practically no suspended solids are detected. Then a period of sludge adaptation to the effluent of the phototreatment is carried out (2 weeks).

Finally, the bioreactors are fed only with the different photo-treated solutions used to study the effect of different photo-Fenton parameters on the biological treatment. The required nutrients for bacterial activity are provided after photo-treatment with a concentrated mineral medium, so that volume remained unchanged. The flow rate is 15 ml h^{-1} (360 ml day^{-1}), and the hydraulic retention time is 12 h. The aeration is about 0.03 L h^{-1} . Samples are taken periodically and analyzed.

RESULTS AND DISCUSSION

Photo-fenton experiments

During the photo-Fenton reaction, degradation process depends simultaneously on the irradiation time and on the amounts of H_2O_2 which are really consumed. In fact, the

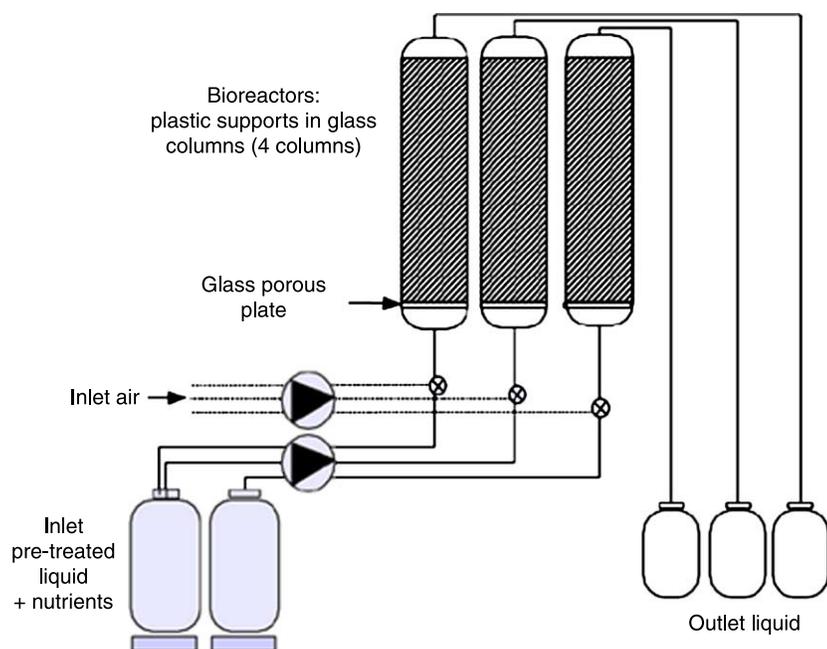


Figure 2 | Experimental setup used for investigation of the photocatalytic biological coupling treatment.

concentration of H_2O_2 was followed in order to avoid any residual amount of H_2O_2 in the photo-treated solution, because H_2O_2 may damage the bacterial cells and thus limit the consecutive biotreatment (Lapertot *et al.* 2007). Thus, to obtain one precise degradation ratio, the exact amount of H_2O_2 was introduced in the solution of 4-CP. Then irradiation was provided until no remaining H_2O_2 was measured. For that reason, in this study, the initial concentrations of H_2O_2 are also the H_2O_2 concentrations really consumed during the photo-Fenton process.

In the photocatalytic pre-treatment it is very important to gather information concerning both chemical and biological characteristics of the solution. TOC analyses, concentration of the 4-CP and its intermediates by HPLC and H_2O_2 concentration were monitored in the course of the photo-Fenton experiments. BOD_5 was also measured at initial and final reaction time.

The main results obtained during the photo-Fenton treatment for different experimental conditions are listed in the Table 2.

As it can be observed in Table 2, the BOD_5 of the treated solutions were increasing with the increase of H_2O_2 concentration (from $0\text{ mgO}_2\text{L}^{-1}$ for the 4-CP not photo-treated (Table 1), to $22\text{ mgO}_2\text{L}^{-1}$ for 4.65 mM of H_2O_2).

The BOD_5/COD ratio, which is the most used parameter to quantify the biodegradability, achieved for this H_2O_2 concentration was 0.32. The threshold value of such ratio for a wastewater to be considered easily biodegradable is 0.4 while a value between 0.2 and 0.4 corresponds to a partially biodegradable wastewater (Farré *et al.* 2006).

Moreover, after 35 min of photo-Fenton treatment with an initial H_2O_2 concentration of 4.65 M , both the 4-Chlorophenol and aromatic intermediates were not detected. TOC removal was around 37% (Table 2). The elimination of the initial bio-recalcitrant compound was required in order to test the biocompatibility of the photo-treated solution. Thus, the experimental

Table 2 | Results of photo-Fenton process applied to 4-CP (0.78 mM) degradation

	Assay 1	Assay 2	Assay 3
Fe^{2+} (mM)	0.36	0.36	0.36
Initial H_2O_2 (mM)	2.33	2.90	4.65
% TOC	17	23	37
Final BOD_5 ($\text{mg O}_2/\text{l}$)	17	18	22
Final COD ($\text{mg O}_2/\text{l}$)	93	84	69
BOD_5/COD	0.18	0.21	0.32
COD/TOC	2.01	1.95	1.97

conditions used for the assay 3 were chosen to feed the biological reactors.

Photochemical–biological coupled treatment: effect of Fenton parameters on the efficiency of biological treatment

Despite the selection of optimal conditions for photo-Fenton process, changes of pH, presence of H_2O_2 and iron in the feed of biological treatment could happen because of operational problems in real applications. For this reason, Fenton parameters selected for this research work were the pH, residual iron and residual hydrogen peroxide.

The bioreactors were operated in continuous mode, whereas the photo-chemical treatment was operated in batch mode. Sequential batches of the photo-Fenton process, using the experimental conditions of assay 3 (Table 2), were carried out so that the input flow rate into the biological reactors was 0.36 L day^{-1} . This flow rate was maintained during at least 33 days.

Photo-Fenton effluents, containing residual iron, were adjusted to selected value of pH (2.5, 3.5, 5.0 or 7), and circulated through the bioreactors to study the effect of this variable on the biological treatment. In other biological experiments, H_2O_2 was added at different concentrations (0, 2.3 and 4.6 mM) to the photo-treated solution in order to know the influence of hydrogen peroxide on the biological treatment.

Table 3 gives the characteristics of different biological experiments which were tested for biocoupling. The influence of the pH (2.5, 3.5, 5.0 and 7.0), the H_2O_2 concentration (0, 2.3 and 4.6 mM) and residual iron were studied.

Figure 3 shows the results obtained with the four bioreactors during an initial period of 11 days with all reactors under the same experimental conditions: reactors fed with pretreated solution at an adjusted pH 7 and

Table 3 | Characteristics of different solutions (a–f) which were tested for bio-coupling

Experimental conditions	Biological experiments					
	a	b	c	d	e	f
pH	7	2.5	3.5	5	7	7
Residual Fe (mM)	0.36	0.36	0.36	0.36	0.36	0.36
Residual H_2O_2 (mM)	0	0	0	0	2.3	4.6

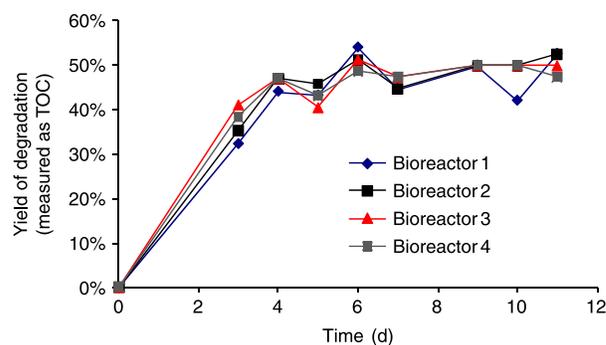


Figure 3 | TOC abatement in the 4 bioreactors during the first 12 days. Reactors feed with pre-treated solution. pH = 7 and $H_2O_2 = 0$.

without H_2O_2 addition (optimal conditions). As it can be observed in Figure 3, a relatively steady-state condition for TOC removal was observed in the columns after 5 days (around 50% of yield of organic matter degradation).

Figure 4 shows the results relating to the influence of the residual H_2O_2 on the biological treatment. In this figure are depicted yields of organic matter degradation (measured as TOC) achieved in three bioreactors, which operated using the experimental conditions of biological experiments *e*, *f* and *a* (Table 3). It can be observed that the presence of this reactive in similar concentrations to that used in the photo-Fenton process (2.3 mM, 4.6 mM) was not negative on the biological activity, since yields of TOC degradation were similar both in experiments with presence of H_2O_2 and in the absence of this Fenton reagent. Average values of 50% of TOC elimination were achieved in the case of H_2O_2 presence at different concentrations in the solutions and for the experiment without residual presence of hydrogen peroxide.

Figure 5 shows the performance of the biological treatment for pre-treated solutions with different pH (2.5, 3.5, 5.0 and 7). In this figure are depicted yields of organic

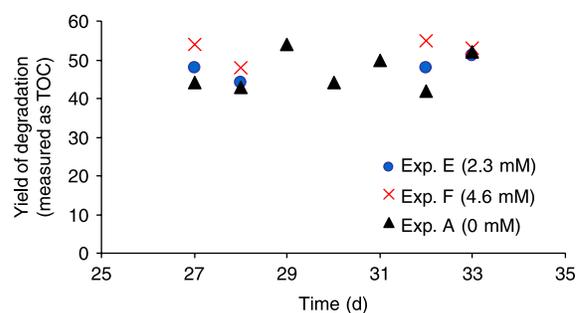


Figure 4 | Influence of residual hydrogen peroxide in the phototreated solutions on the performance of biological treatment.

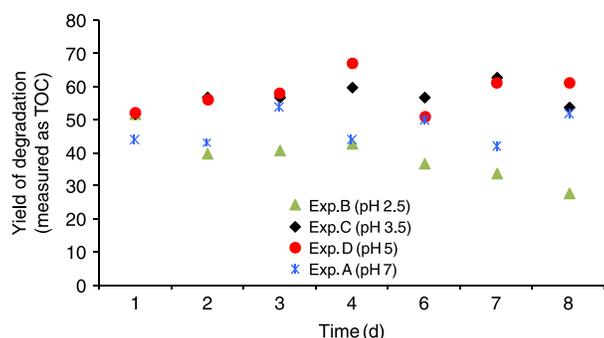


Figure 5 | Influence of the pH on the performance of the biological treatment.

matter degradation (measured as TOC) achieved for each bioreactors, which were operating using the experimental conditions of biological experiments *b*, *c*, *d* and *a* (Table 3).

As it can be observed in Figure 5, the performance of the biological process is adequate in the range of pH 3.5–7 during an operation time of 8 days. These results indicate that in case of accident of pH regulation the fixed biomass present in our bioreactors has a good resistance to pH shocks for a period of several days without affecting the coupled photo-Fenton–biological system.

In the case of the biological experiment *b* (Table 3, Figure 5), in which a phototreated solution with a pH of 2.5 was used, the bioreactor began to operate in an inadequate way and the yield of organic matter degradation (measured as TOC) decreased until 20%. After this biological experiment, aqueous solutions of glucose were fed to the bioreactor and the results revealed that many microorganisms could degrade this easily biodegradable substrate so the recovery of the biological system was achieved.

The effect of the residual iron (20 mg L^{-1}) on the biological process was not negative since the optimal concentration used for the photo-Fenton treatment was still low enough to ensure non-inhibitory effects (Oller et al. 2007).

CONCLUSIONS

This research work shows that a coupled photo-Fenton–biological system applied to treatment of 4-chlorophenol solutions operate adequate in a wide range of operational conditions. The study of the influence of different photo-Fenton parameters, such as pH variations and residual iron

and hydrogen peroxide, on the pack-bed bioreactor biological indicate the following main results.

- Biological process works in the range of pH 3.5–7 during an operation time of 8 days. These results indicate that in case of pH regulation failure, the fixed biomass present in our bioreactors has a good resistance to pH shocks for a period of several days without affecting the coupled photo-Fenton–biological system.
- Presence of residual H_2O_2 on the biological treatment in similar concentrations to that used in the photo-Fenton process (2.3 mM, 4.6 mM) is not negative on the biological activity.
- The effect of residual iron (20 mg L^{-1}) on the biological process was not negative since the optimal concentration used for the photo-Fenton treatment was still low enough to ensure non-inhibitory effects.

ACKNOWLEDGEMENTS

The financial support obtained from the European Commission is acknowledged (INNOWATECH project, contract no 036882, FP6-2005-Global-4, SUSTDEV-2005-3.II.3.2).

REFERENCES

- Bacardit, J., Stötzner, J., Chamarro, E. & Esplugas, S. 2007 Effect of salinity on the photo-Fenton process. *Ind. Eng. Chem. Res.* **46**, 7615.
- Bandara, J., Pulgarin, C., Kiwi, J. & Péringier, P. 1997 Chemical (photo-activated) coupled biological homogeneous degradation of *p*-nitro-toluene-sulfonic acid in flow reactor. *J. Photochem. Photobiol. A Chem.* **111**, 253–260.
- Cleresci, L. S., Greenberg, A. E. & Trussell, R. R. 2005 *Standard Methods for the Examination of Waste Water*, 21st edition. American Public Health Association, Maryland, USA.
- EC Decision 2455/2001/EC of the European Parliament and of the Council of November 20, 2001 establishing the list of Priority substances in the field of water policy and amending Directive 2000/60/EC.
- Essam, T., Zilouei, H., Amin, M. A., Mattiasson, B. & Guieysse, B. 2006 Sequential UV-biological degradation of chlorophenols. *Chemosphere* **63**, 277–284.
- Farré, M. J., Doménech, X. & Peral, J. 2006 Assessment of photo-Fenton and biological treatment coupling for Diuron and Liuron removal from water. *Water Res.* **40**, 2533–2540.

- Hayward, K. 1998 Drinking water contaminant hit-list for US EPA. *Water* **21**, September–October, 4.
- Herrera, F., Pulgarin, C., Nadtochenko, V. & Kiwi, J. 1998 Accelerated photo-oxidation of concentrated *p*-coumaric acid in homogeneous solution. Mechanistic studies, intermediates and precursors formed. *Appl. Catal. B Environ.* **17**, 141–156.
- Keith, L. H. & Telliard, W. A. 1979 Priority Pollutants: a prospective view. *Environ. Sci. Technol.* **13**, 416–424.
- Lapertot, M., Ebrahimi, S., Dazio, S., Rubinelli, A. & Pulgarin, C. 2007 Photo-fenton and biological process degradation of a mixture of pesticides. *J. Photochem. Photobiol. A Chem.* **186**, 34–40.
- Lewandowski, G. A. & DeFilippi, L. J. 1998 Introduction to microbial degradation of aqueous waste and its application using a fixed-film reactor. In: Lewandowski, G. A. & DeFilippi, L. J. (eds) *Biological Treatment of Hazardous Wastes*. John Wiley and Sons, Inc., New York, USA.
- Oller, I., Malato, S., Sanchez-Perez, J. A., Gernjak, W., Maldonado, M. I., Perez-Estrada, L. A. & Pulgarin, C. 2007 A combined solar photocatalytic-biological field system for the mineralization of an industrial pollutant at pilot scale. *Catal. Today* **122**, 150–159.
- Ormad, M. P., Mosteo, R., Ibarz, C. & Ovelleiro, J. L. 2006 Multivariate approach to the photo-fenton process applied to the degradation of winery wastewaters. *Appl. Catal. B Environ.* **66**, 58–63.
- Parra, S., Sarria, V., Malato, S., Peringer, P. & Pulgarin, C. 2000 *Appl. Catal. B Environ.* **27**, 153–168.
- Pera-Titus, M., García-Molina, V., Baños, M. A., Giménez, J. & Esplugas, S. 2004 Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Appl. Catal. B Environ.* **47**, 219–256.
- Pignatello, J. J., Oliveros, E. & Mackay, A. 2006 Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **36**, 1–84.
- Pulgarin, C. & Kiwi, J. 1996 Photocatalytic and electrocatalytic pretreatment of industrial non-biodegradable pollutants and pesticides. *Chimia* **50**, 50–55.
- Pulgarin, C., Invernizzi, M., Parra, S., Sarria, V., Polania, R. & Peringer, P. 1999 *Catal. Today* **54**, 341–352.
- Ren, S. & Frymier, P. D. 2002 Estimating the toxicities of organic chemicals to bioluminescent bacteria and activated sludge. *Water Res.* **36**, 4406–4414.
- Sarria, V., Parra, S., Adler, N., Peringer, P., Benitez, R. & Pulgarin, C. 2002 Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. *Catal. Today* **76**, 301–315.
- Sarria, V., Deront, M., Péringer, P. & Pulgarin, C. 2003 Degradation of a biorecalcitrant dye precursor present in industrial wastewaters by a new integrated iron (III) photoassisted-biological treatment. *Appl. Catal. B Environ.* **40**(3), 231–246.
- Yuranova, T., Mosteo, R., Bandara, J., Laub, D. & Kiwi, J. 2006 Self-cleaning cotton textiles surfaces modified by photoactive SiO₂/TiO₂ coating. *J. Mol. Catal. A Chem.* **244**, 160–167.