

Enhanced photo-Fenton Process for Tetracycline Degradation using Efficient Hydrogen Peroxide Dosage

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Abstract

The remediation of water solutions containing Tetracycline antibiotic (TC) using photo-Fenton treatments has received scarce attention in the literature. However TC deserves attention due to its condition of emerging contaminant. In this work, TC oxidation in water solutions (12 L, 40 mg L⁻¹) by means of photo-Fenton reaction under variable hydrogen peroxide dosage is investigated. This shows a more efficient use of the hydroxyl radicals produced in the reaction medium and enhances treatment performance. First, a suitable range of Fenton reagent loads is determined in a preliminary study. The hydrogen peroxide dosage is parameterized through two variables: the initial release of the total load, y_0 (kick-off), and the time t_{ini} at which the continuous dosage of the rest of the load starts. Hence, a design of experiments (2²) can be used to characterize the performance of the process under different hydrogen peroxide dosage protocols. The results obtained this way show that total TC remediation is attained in all the cases studied, but alike amounts of hydrogen peroxide lead to total mineralization only when the dosage scheme is conveniently tuned. Therefore, the photo-Fenton treatment has proved to be effective in removing TC from water solutions, and the opportunity for an efficient dosage to reduce the requirements of hydrogen peroxide has also been confirmed.

Keywords: Tetracycline antibiotic, emerging contaminants, photo-Fenton treatment, hydrogen peroxide dosage, design of experiments.

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Highlights

- Tetracycline in water solutions is shown to be totally degraded via photo-Fenton treatment
- Subject to dosage, a H₂O₂ load can mineralize a tetracycline solution to different extents
- H₂O₂ dosage is modeled via two parameters, upon which a design of experiments is proposed
- Design of experiments dosage conditions yield mineralization rates ranging from 77% to almost 100%
- If conveniently dosed, stoichiometric H₂O₂ loads can achieve total mineralization

1. Introduction

In recent years, a new group of contaminants called emerging contaminants has been detected in water sources. Although they are found in very low concentrations (in the order of ng- $\mu\text{g L}^{-1}$) they can become a real environmental problem because of their high persistence and ecotoxicity [1, 2]. Among these emerging contaminants are pharmaceuticals and personal care products (PPCPs) that can act as endocrine disruptors and affect bacteria used in conventional water treatments [3].

In particular, tetracyclines (TCs) are broad-spectrum antibiotics with activity against gram-positive and gram-negative bacteria. The presence of such antibiotics in the environment is mainly due to their discharge through excretion whether or not metabolized. As conventional treatments cannot be expected to process this kind of contaminants, they come to appear in surface water, groundwater and even in drinking water, developing antibiotic-resistant pathogens, among several other environmental issues [3-5]. According to Wang et al. [6] they have been detected at concentrations at 0.07-1.34 $\mu\text{g L}^{-1}$ in surface water samples.

In the last thirty years, advanced oxidation processes (AOPs) have acquired increasing interest as an option either to remediate recalcitrant contaminants before or after conventional treatments [7-9]. AOPs consist in the in situ generation of highly oxidant species to degrade organic matter, and have shown to provide excellent results, especially those processes based on the use of the Fenton reagent.

Fenton and related processes (photo-enhanced Fenton process, electro-Fenton, sono-Fenton and so on) have proved to be efficient in mineralizing antibiotics [3, 5, 10, 11].

Tetracycline degradation by means of AOPs has been investigated in the past, especially by using UV and UV/H₂O₂ treatments, and heterogeneous photocatalysis, (contaminant concentrations ranging from 10-100 mg L⁻¹). UV has shown to be effective in degrading this contaminant and the presence of H₂O₂ has revealed to increase TC degradation and mineralization rates [9, 12-45]. Heterogeneous photocatalysis with TiO₂ has also been investigated, and a lower performance with respect to UV and UV/H₂O₂ processes has been reported [8, 16]. Electrochemical processes have also shown to be effective for TC degradation [17, 18]. Conversely, TC degradation via photo-Fenton process has received scarce attention, although TC is among the components of some wastewaters whose photo-Fenton treatment has been investigated [19] and the research by Rossi and Nogueira [5] reported total remediation of 24 mg L⁻¹ TC solutions.

In Fenton processes, hydroxyl radicals are produced by the reaction between hydrogen peroxide and a ferrous salt [20]. In the specific case of photo-Fenton reaction, an external source of energy (UV irradiation) can enhance the process by accelerating iron ions to be regenerated (from Fe³⁺ to Fe²⁺) and recycled [21]. However, since the hydroxyl radical is extremely unstable and non-selective, it is frequently scavenged by undesired secondary reactions. This indicates the convenience to continuously produce hydroxyl radicals in the reaction media instead of using high hydrogen peroxide concentrations at the beginning of the process [22].

Recent efforts have been devoted to the use of continuous or semi-continuous hydrogen peroxide dosage for reducing the scavenging of hydroxyl radicals, thus reducing costs and environmental impact as well [21, 23]. Examples of this are the work by Chu et al. [24], who proposed a stepwise dosage of hydrogen peroxide that improved mineralization; the work by Zazo et al. [25], who applied a continuous dosage protocol to the Fenton treatment to increase abatement of TOC with the same overall H₂O₂ consumption; and the work by Prato-Garcia and Buitrón [26], who addressed the decolorization of azo dye mixtures by means of two different continuous dosage strategies that improved effluent quality in terms of toxicity and biodegradability. Hydrogen peroxide dosage has

been investigated for Fenton treatments aimed at increasing the efficiency of the remediation of solutions of other six selected antibiotics [27]. However, regarding the oxidation of TC antibiotic in water solutions via photo-Fenton treatment, to the best of the authors' knowledge, no study has been reported on the influence of hydrogen peroxide dosage.

More recently, Yamal-Turbay et al. [28] proposed a practical parameterization of hydrogen peroxide dosage protocol that allowed setting an easy design of experiments to characterize the influence of hydrogen peroxide dosage on the performance of a photo-Fenton treatment. This technique was tested in the remediation of coffee solutions and led to the determination of more efficient dosage conditions for hydrogen peroxide and enhanced process performance. This work aims to apply this systematic dosage protocol for improving the performance of the photo-Fenton treatment of TC solutions in water.

2. Methods

2.1 Materials

95% purity TC hydrochloride from Sigma Aldrich was purchased to prepare 40 mg L⁻¹ solutions in tap water. Fenton reagents: hydrogen peroxide 33% w/v (Panreac) and 7-hydrated iron (II) sulfate (Merck) were used as received. HCl (J.T. Baker) and NaOH (Panreac) 1 M were used for automated pH adjustment.

Oxalic acid 0.01 M (Panreac) prepared in filtered milli Q grade water and J.T. Baker ultragradient HPLC acetonitrile and methanol were used as HPLC mobile phases, while a stock of ammonium metavanadate (Riedel-de-Haën) 0.062 M in H₂SO₄ (Panreac) 0.58 M according to Nogueira et al. [29] was kept refrigerated for hydrogen peroxide measurement.

2.2 Pilot plant description

The photochemical pilot plant consists in a 12 L system: glass reservoir and piping system. The light source is a 230 W medium pressure mercury lamp UV TQ718 (irradiating from 300 to 550 nm)

placed in a glass cooling jacket in the center of the reservoir. The incident photon flux, determined by potassium ferrioxalate actinometry [30], was 3.4033×10^{-5} Einstein s^{-1} .

The system is provided with a centrifugal pump which keeps a recirculation flow of 12 L min^{-1} . The reaction pH was maintained at 2.7 ± 0.1 by using a proportional-integral-derivative (PID) controller. Figure 1a shows a diagram of the pilot plant.

2.3 Analytical methods

Process performance was evaluated by withdrawing aliquots from the pilot plant and measuring the following variables at regular time intervals:

- Total organic carbon (TOC) concentration was measured by means of a Shimadzu $V_{\text{CHS/CSN}}$ TOC analyzer.
- TC concentration was determined via HPLC, using an Agilent 1200 series with UV-DAD array detector. The chromatographic conditions and data analysis were performed using the Agilent Chem-Station (Rev.B.04.06 SP1[647]) software. The chromatographic column was a $5 \mu\text{m}$ $4.6 \times 150 \text{ mm}$ Zorbax Eclipse XDB-C18 (Agilent Technologies), maintained at 30°C , and the diode array detector was set at 271 nm . $20 \mu\text{L}$ samples, injected by a manual injector, were eluted by a mixture (70% 0.01 M oxalic acid, 10% methanol and 20% acetonitrile) flowing at 1.0 mL min^{-1} [31]. Tetracycline retention time under these conditions was 2.4 minutes. A five-level calibration curve (range $2\text{-}30 \text{ mg L}^{-1}$) was used for TC quantification.
- H_2O_2 concentration was measured by a UV-vis spectrophotometer Hitachi U-2001 after reaction with ammonium metavanadate, following the technique proposed by Nogueira et al. [29].

2.4 Hydrogen peroxide dosage definition

The continuous dosage of H_2O_2 was executed by means of a peristaltic pump (Watson Marlow 300 series OEM) programmed from the pilot plant SCADA. The dosage protocol was previously proposed and stated [28] and is characterized (Eq. 1) by the fraction of the total dose of H_2O_2 added initially, y_0 ,

the dosage interval, Δt_{add} , and the time at which the dosage starts, t_{ini} . Figure 1b shows a graphical representation of the addition protocol.

$$y(t) = \frac{v_D(t)}{v_D^\infty} = \begin{cases} 0 & \text{if } t < 0 \\ y_0 & \text{if } 0 \leq t < t_{ini} \\ y_0 + \left(\frac{1 - y_0}{\Delta t_{add}} \right) (t - t_{ini}) & \text{if } t_{ini} \leq t < t_{ini} + \Delta t_{add} \\ 1 & \text{if } t_{ini} + \Delta t_{add} \leq t < TS \end{cases} \quad (1)$$

After a preliminary study which will be explained in further sections, the total amount of H₂O₂ was fixed to 858 mg, which corresponds to an equivalent concentration of 71.5 mg L⁻¹. The treatment span and the dosage interval were also fixed ($TS=90$ min; $\Delta t_{add}=30$ min). Hence, the remaining two degrees of freedom (y_0, t_{ini}) were used in the design of experiments. The quantitative performance index selected to rank the output of the assays and to discuss the results is the conversion attained at TS , defined as follows:

$$\xi^{TS} = 1 - \frac{C_{TS}^{TOC}}{C_0^{TOC}} \quad (2)$$

3. Results and discussion

3.1. Preliminary assays

3.1.1. Reagent doses

As mentioned in the introduction, the concentrations investigated in previous works concerning TC degradation by means of photolysis and photocatalysis processes ranged between 10 and 300 mg L⁻¹ [4, 8, 13, 16], while Rossi and Nogueira [5] proved that photo-Fenton process can be successfully applied for the degradation of 24 mg L⁻¹ TC solutions with hydrogen peroxide and ferrous iron initial concentrations ranging from 35 to 680 mg L⁻¹ and 5.6 and 11 mg L⁻¹, respectively. According to this information and taking into account TOC analyzer sensibility, TC concentration was fixed at 40 mg L⁻¹, which corresponds to a TOC concentration of 23 mg L⁻¹ and requires a stoichiometric H₂O₂ concentration of 150 mg L⁻¹.

A 2² factorial design of experiments (DOE) with star points was performed to decide Fenton reagent doses. It was important to identify a dose which permits a compromise between degradation and dosage interest. For that aim, Fe²⁺ dose was centered at 5 mg L⁻¹ (10 mg L⁻¹ is the maximum legal value in effluents in Spanish legislation [32]), having minimum and maximum values 2 and 8 mg L⁻¹, respectively.

Regarding H₂O₂ load, this ranged between 9% and 90% of the stoichiometric amount given by the TC oxidation just by means of hydrogen peroxide, which is taken as a reference. Sub-stoichiometric hydrogen peroxide loads can be used to ease the identification intermediate species at the early stages of the reaction [33]; furthermore, sub-stoichiometric loads can be enough for total TC oxidation since hydrogen peroxide is not the only source of oxygen [21, 34]. Minimum and maximum values of the H₂O₂ load were set at 14.3 and 128.7 mg L⁻¹, having a center value of 71.5 mg L⁻¹, which corresponds to a 48% of the stoichiometric amount. Figure 2a presents DOE results considering ξ^{TS} as the system response.

Low iron loads (2 mg L⁻¹) provide degradation rates around 55% despite H₂O₂ dose (red line). On the contrary, higher iron values (5 or 8 mg L⁻¹) noticeably increase response values as H₂O₂ doses increase. However, 5 mg L⁻¹ iron loads lead to higher TOC degradation than 8 mg L⁻¹ for equal H₂O₂ amounts (lines blue and green). Thus, 5 mg L⁻¹ iron loads offer more efficient use of the hydroxyl radicals generated in the system. According to this, iron dose was set at 5 mg L⁻¹.

Finally, a hydrogen peroxide dose was set at 71.5 mg L⁻¹ because higher values, when combined with 5 mg L⁻¹ iron doses provide too fast TOC reduction, which complicates the evaluation of the effect of reagent dosage on degradation. In brief, from here on, the following concentrations are used:

- Tetracycline initial concentration = 40 mg L⁻¹
- Hydrogen peroxide equivalent concentration = 71.5 mg L⁻¹
- Iron (II) initial concentration = 5 mg L⁻¹

3.1.2. Blank assays

A set of blank assays was initially performed in order to evaluate the influence of each separate reagent on TOC and TC degradation, which are next presented. Figure 2b shows the evolution of TOC, H₂O₂ and TC concentrations for UV treatment, UV/H₂O₂, Fenton and photo-Fenton, involving the previously stated reagent doses when applied.

Mineralization by means of UV treatment only reaches 35%, UV/H₂O₂ and Fenton allow almost 60%, and the photo-Fenton process may reach 77%. TC is completely degraded in all the cases where H₂O₂ is present, being the degradation faster when the ferrous salt is added. On the contrary, only a 40% of TC is degraded by solely using UV irradiation (90 min treatment). Both TC and TOC reduction rates obtained without using H₂O₂ are comparatively poor. However, it is important to bear in mind that these rates indicate that, to a non-negligible extent, H₂O₂ may not be the sole responsible of the complete oxidation of organic matter.

Once established that the photo-Fenton process is capable of degrading TC and mineralize organic matter, H₂O₂ dosage was investigated in order to determine to which extent process efficiency can be improved given the same reagent loads.

3.2. DOE for dosage characterization

A design of experiments considering the dosage parameters y_0 and t_{ini} (eq.1) and the response ξ^{TS} was applied; the earliest sample time at which TC is not detected (t^{TC}) was also included as a response. Table 1 lists the levels and results of the planned assays according to a 2² DOE with start points and three center points for statistical validity; minimum and maximum factors were set at 10 and 30% for y_0 and 0 and 30 minutes for t_{ini} . Reference experiments were included in the study.

Figure 3a shows the results of the central experiment of the design, which was repeated six times. Average values are presented along with the corresponding standard deviations. Total remediation of the sample is shown to be achieved with these conditions. Regarding TC degradation, it was achieved within 10 minutes treatment.

From this point on, experiments are named according to the following nomenclature: “Experiment-code- y_0 - t_{ini} ”. Assay R corresponds to the reference experiment (no dosage protocol).

Figure 3b compares the evolution of TOC and TC concentrations for the central assays ($y_0=20\%$; $t_{ini}=15$ min), an assay without kick-off (experiment code L, $y_0=0\%$; $t_{ini}=0$ min), and the reference assay. The performance obtained is analogous to that obtained by previous studies using caffeine [28].

Only 77% mineralization is achieved without dosage. However, the proposed scheme, when conveniently tuned, shows that it is possible to reach up to almost total mineralization (98%), which corresponds to 27 percent points of improvement. According to Prato-Garcia and Buitrón [26], this may be explained because when the entire reagent dose is added at once, the excess of H_2O_2 promotes secondary reactions that scavenge hydroxyl radicals and “waste” them. Dosage allows reducing this excess and having a more efficient dedication of hydroxyl radicals to degrading organic matter [22, 25, 28].

Regarding TC remediation, table 1 shows the earliest sample time (t^{TC}) at which TC is not detected and total degradation is assumed. The slowest degradation is observed in experiments B and J, for which t^{TC} increases up to 45 and 30 minutes respectively, while for the rest of the assays t^{TC} is below 15 minutes. This behavior can be explained because of the combination of low initial hydrogen peroxide doses (y_0), which is rapidly exhausted and causes the process to stop, and the late dosage (t_{ini}), which slows the process down; actually, better performance of experiment J compared to assay B obeys to sooner t_{ini} despite lower y_0 .

Figure 4 shows the relation between conversion at TS , ξ^{TS} , and the time at which total degradation is assumed, t^{TC} . This confirms the opportunity to improve the treatment outcome by adjusting the dosage parameters. When the reagent is dosed proportionally without kick-off addition (experiment L), an improvement of 18 percent points is possible; furthermore, both objectives, maximizing mineralization and minimizing time for degrading TC, are achieved simultaneously. That is the case of experiment C, which is the closest to the low right corner of the plot.

Regarding the evident interaction between both factors y_0 and t_{ini} these results also indicate the higher significance of the latter. When continuous dosage starts soon, better performance is achieved despite y_0 ; conversely, low y_0 values may require starting dosage at earlier t_{ini} values. Further data on the influence of low y_0 values on TC degradation are given in Figure 5. Compared to assay J ($t_{ini}=15$

min), the higher y_0 value of new experiment P_8_15 (8%) produces no performance changes; however, the lower y_0 value of new experiment Q_4_15 (4%) results in hydrogen peroxide exhaustion and the process interruption until more reagent is dosed after 15 minutes.

4. Conclusions

The oxidation of TC antibiotic in water solutions by means of the photo-Fenton treatment was investigated. The treatment was applied to 12 L of 40 mg L⁻¹ tetracycline samples with total reagent doses of 71.5 mg L⁻¹ hydrogen peroxide (48% of stoichiometric dose) and 5 mg L⁻¹ Fe²⁺ (half the legal limit in wastewaters in Spain). These conditions achieved total TC remediation and to produce up to 77% solution mineralization within the reaction span studied.

Hydrogen peroxide dosage was also investigated in order to improve process performance. Since excess hydrogen peroxide fosters scavenging reactions, dosage is considered to provide the conditions for reducing this unsolicited effect. A dosage protocol introduced in a previous work was applied to the study of the degradation of TC.

The systematic parameterization of the dosage led to a DOE for determining the treatment outcome for a given set of assays. Hence, given this fixed H₂O₂ load, treatment performance was shown to be able to improve total mineralization (up to 22.6 percent points) when dosage parameters were conveniently adjusted.

The efficient use of hydrogen peroxide, via dosage, has revealed to significantly improve the performance of the treatment of water solutions containing TC by cutting the H₂O₂ demand and reducing the cost of photo-Fenton treatments. This work has also shown that the H₂O₂ demand can be reduced quite below the stoichiometric value, which suggests the importance of other oxygen sources in the photo-Fenton treatment. This additional aspect and its relation with dosage deserve further investigation.

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References

- [1] N. Klammerth, L. Rizzo, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba, Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO₂, *Water Res.* 44:2 (2010), 545-545.
- [2] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination - A review, *Sci. Total Environ.* 409 (2011) 4141–4166
- [3] V. Homem, L. Santos, Degradation and removal of antibiotics from aqueous matrices. A review, *J. Environ. Manag.* 92 (2011) 2304-2347
- [4] S. Jiao, S. Zheng, D. Yin, L. Wang, L. Chen, Aqueous photolysis of tetracycline and toxicity of photolytic products to luminescent bacteria, *Chemosphere* 73 (2008) 377–382
- [5] I. Rossi, R.F.P. Nogueira, Degradation of tetracycline by photo-Fenton process—Solar irradiation and matrix effects, *J. Photoch. Photob. A.*, 187 (2007) 33-39.
- [6] P. Wang, Y.L. He, C.H. Huang, Reactions of tetracycline antibiotics with chlorine dioxide and free chlorine, *Water Res.* 45 (2011) 1838-1846
- [7] S. Kaniou, K. Pitarakis, I. Barlagianni, I. Poullos, Photocatalytic oxidation of sulfamethazine, *Chemosphere* 60 (2005) 372–380
- [8] C. Reyes, J. Fernández, J. Freer, M.A. Mondaca, C. Zaror, S. Malato, H.D. Mansilla, Degradation and inactivation of tetracycline by TiO₂ photocatalysis, *J. Photochem. Photobiol., A.* 184 (2006) 141–146

- [9] J.J. López-Peñalver, M. Sánchez-Polo, C.V. Gómez-Pacheco, J. Rivera-Utrilla, Photodegradation of tetracyclines in aqueous solution by using UV and UV/H₂O₂ oxidation processes, *J. Chem. Technol. Biotechnol.* (2010) DOI 10.1002/jctb.2435
- [10] M. Pérez, F. Torrades, J.A. García-Hortal, X. Domènech, J. Peral, Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, *Appl. Catal. B.*, 36 (2002) 63–74
- [11] A.G. Trovó, R.F.P. Nogueira, A. Agüera, A.R. Fernandez-Alba, S. Malato, Degradation of the antibiotic amoxicillin by photo-Fenton process - Chemical and toxicological assessment, *Water Res.* 45 (2011) 1394-1402.
- [12] K.H. Wammer, M.T. Slattery, A.M Stemig, J.L. Ditty, Tetracycline photolysis in natural waters: Loss of antibacterial activity, *Chemosphere* 85 (2011) 1505–1510
- [13] C.V. Gómez-Pacheco, M. Sánchez-Polo, J. Rivera-Utrilla, J.J. López-Peñalver, Tetracycline degradation in aqueous phase by ultraviolet radiation, *Chem. Eng. J.* 187 (2012) 89-95
- [14] I. Kim, H. Tanaka, Photodegradation characteristics of PPCPs in water with UV treatment, *Environ. Int.* 35 (2009) 793–802
- [15] F. Yuan, C. Hu, X. Hu, D. Wei, Y. Chen, J. Qu, Photodegradation and toxicity changes of antibiotics in UV and UV/H₂O₂ process, *J. Hazard. Mater.* 185 (2011) 1256–1263
- [16] V. Maroga Mboula, V. Héqueta, Y. Gru, R. Colin, Y. Andrès, Assessment of the efficiency of photocatalysis on tetracycline biodegradation, *J. Hazard. Mater.* 209-210 (2012) 355-364
- [17] J. Wu, H. Zhang, N. Oturan, Y. Wang, L. Chen, M.A. Oturan, Application of response surface methodology to the removal of the antibiotic tetracycline by electrochemical process using carbon-felt cathode and DSA (Ti/RuO₂-IrO₂) anode, *Chemosphere* 87:6 (2012) 614-620
- [18] J. Jeong, W. Song, W.J. Cooper, J. Jung, Degradation of tetracycline antibiotics: Mechanisms and kinetic studies for advanced oxidation/reduction processes, *Chemosphere* 78 (2010) 533–540
- [19] J.L. Rodríguez-Gil, M. Catalá, S. González Alonso, R. Romo Maroto, Y. Valcárcel, Y. Segura, R. Molina, J.A. Melero, F. Martínez, Heterogeneous photo-Fenton treatment for the reduction

of pharmaceutical contamination in Madrid rivers and ecotoxicological evaluation by a miniaturized fern spores bioassay, *Chemosphere* 80 (2010) 381–388

[20] F. Haber, J. Weiss, The catalytic decomposition of hydrogen peroxide by iron salts, *Proc. Roy. Soc. A.* 134 (1934) 332.

[21] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, *Crit. Rev. Environ. Sci. Technol.* 36:1 (2006) 1-84

[22] I. Gulkaya, A. Surucu, F. Dilek, Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater, *J. Hazard. Mater. B.* 136 (2006) 763-769.

[23] N. H. Ince, "Critical" effect of hydrogen peroxide in photochemical dye degradation, *Water Res.* 33 (1999) 1080-1084.

[24] W. Chu, K.H. Chan, C.Y. Kwan, K.Y. Choi, Degradation of atrazine by modified stepwise-Fenton's processes, *Chemosphere* 67 (2007) 755-761

[25] J.A. Zazo, J.A. Casas, A.F. Mohedano, J.J. Rodríguez, Semicontinuous Fenton oxidation of phenol in aqueous solution. A kinetic study, *Water Res.* 43 (2009) 4063-4069

[26] D. Prato-Garcia, G. Buitrón, Evaluation of three reagent dosing strategies in a photo-Fenton process for the decolorization of azo dye mixtures, *J. Hazard. Mat.* 217–218 (2012) 293–300

[27] W. Ben, Z. Qiang, X. Pan, M. Chen, Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent, *Water Res.* 43 (2009) 4392–4402

[28] E. Yamal-Turbay, M. Graells, M. Pérez-Moya, Systematic Assessment of the Influence of Hydrogen Peroxide Dosage on Caffeine Degradation by photo-Fenton Process, *Ind. Eng. Chem. Res.* 51:13 (2012) 4770

[29] R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate, *Talanta* 66 (2005) 86-91

[30] S.L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973, section 13

[31] J. Zhou, X. Xue, Y. Li, J. Zhang, F. Chen, L. Wu, L. Chen, J. Zhao, Multiresidue determination of tetracycline antibiotics in propolis by using HPLC-UV detection with ultrasonic-assisted extraction and two-step solid phase extraction, *Food Chem.* 115 (2009) 1074–1080

[32] DOGC núm. 3894, DECRET 130/2003, de 13/05/2003, (29.5.2003). (URL: <http://www.gencat.cat/diari/3894/03127147.htm>, accessed 10/08/2011)

[33] M. Munoz, Z.M. de Pedro, J.A. Casas, J.J. Rodriguez, Triclosan breakdown by Fenton-like oxidation, *Chem. Eng. J.* 198-199 (2012) 275-281

[34] Z. Frontistis, N.P. Xekoukoulotakis, E. Hapeshi, D. Venieri, D. Fatta-Kassinos, D. Mantzavinos, Fast degradation of estrogen hormones in environmental matrices by photo-Fenton oxidation under simulated solar radiation, *Chem. Eng. J.* 178 (2011) 175–182