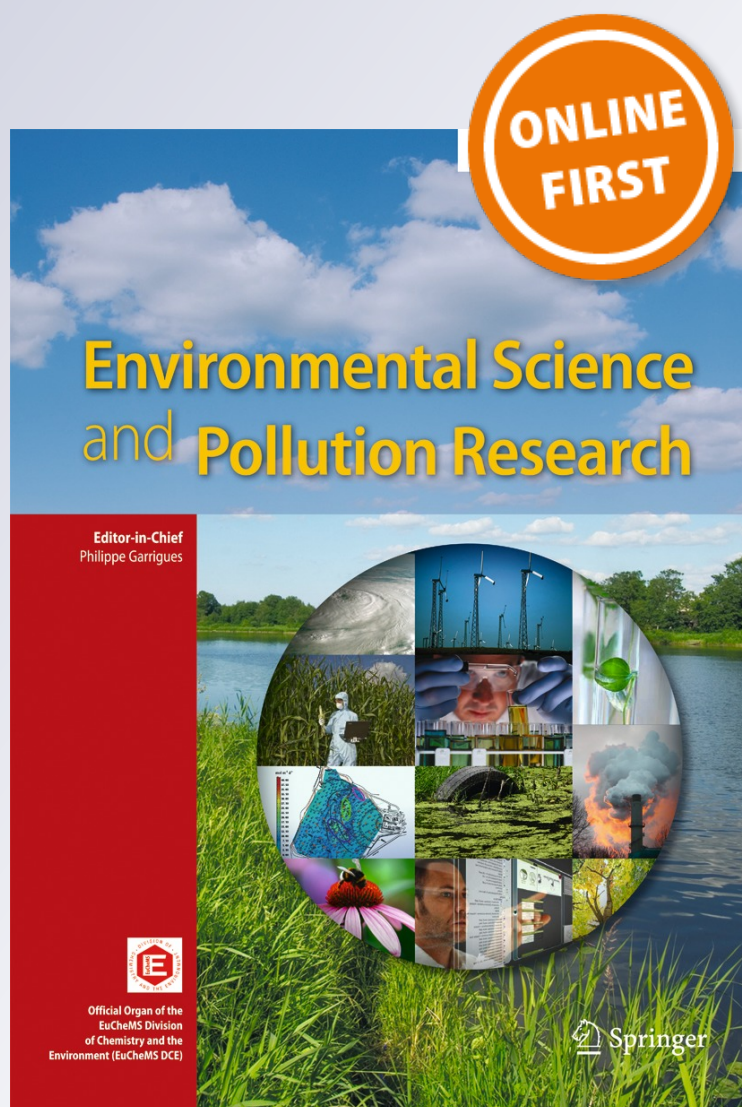# Photonic efficiency of the photodegradation of paracetamol in water by the photo-Fenton process

E. Yamal-Turbay, E. Ortega, L. O. Conte, M. Graells, H. D. Mansilla, O. M. Alfano & M. Pérez-Moya

Springer

ADVANCED OXIDATION TECHNOLOGIES: ADVANCES AND CHALLENGES IN IBEROAMERICAN COUNTRIES

Photonic efficiency of the photodegradation of paracetamol in water by the photo-Fenton process

E. Yamal-Turbay · E. Ortega · L. O. Conte · M. Graells · H. D. Mansilla · O. M. Alfano · M. Pérez-Moya

Abstract An experimental study of the homogeneous Fenton and photo-Fenton degradation of 4-amidophenol (paracetamol, PCT) is presented. For all the operation conditions evaluated, PCT degradation is efficiently attained by both Fenton and photo-Fenton processes. Also, photonic efficiencies of PCT degradation and mineralization are determined under different experimental conditions, characterizing the influence of hydrogen peroxide (H_2O_2) and Fe(II) on both contaminant degradation and sample mineralization. The maximum photonic degradation efficiencies for 5 and 10 mg L^{-1} Fe(II) were 3.9 (H_2O_2=189 mg L^{-1}) and 5 (H_2O_2=378 mg L^{-1}), respectively. For higher concentrations of oxidant, H_2O_2 acts as a "scavenger" radical, competing in pollutant degradation and reducing the reaction rate. Moreover, in order to quantify the consumption of the oxidizing agent, the specific consumption of the hydrogen peroxide was also evaluated. For all operating conditions of both hydrogen peroxide and Fe(II) concentration, the consumption values obtained for Fenton process were always higher than the corresponding values observed for photo-Fenton. This implies a less efficient use of the oxidizing agent for dark conditions.

E. Yamal-Turbay (✉) · E. Ortega · M. Graells · M. Pérez-Moya
Escola Universitària d'Enginyeria Tècnica Industrial de Barcelona, c/ Comte d'Urgell 187, 08036 Barcelona, Spain
e-mail: evelyn.yamal@gmail.com

H. D. Mansilla
Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile

L. O. Conte · O. M. Alfano
INTEC, Universidad Nacional del Litoral and CONICET, Santa Fe, Argentina

Introduction

Emerging contaminants (ECs) have been receiving increasing attention during the last decades, and a lot of effort has been devoted to remove them from wastewaters before their accumulation becomes a real environmental problem. Many pharmaceuticals and personal care products (PPCPs) are among this group, and they are acknowledged to interfere with natural processes in the ecosystems and to have harmful effects over animal or human health (Gültekin and Ince 2007).

Conventional water treatment plants are not designed to remediate this type of recalcitrant contaminants, and they have been detected in natural and even potable waters in the order of ng-μg/L (Broséus et al. 2009; Petróvic et al. 2003; Becerril 2009). Advanced oxidation processes (AOPs), consisting in the in situ generation of powerful oxidant hydroxyl radicals (HO•), can be used before or after conventional treatment plants in order to eliminate ECs from wastewaters and even to reach total mineralization when ideal conditions are provided (Pignatello et al. 2006).

Paracetamol (acetaminophen or 4-amidophenol, PCT from this point on) is a widely used analgesic, anti-inflammatory and antipyretic, reported as the most popular non-opioid analgesic sold in Spain in recent years (Martínez Bueno et al. 2012). It has been found in European Sewage Treatment Plants in concentrations around 6 μg L^{-1} (Ternes 1998). Although high removal rates (99 %) may be attained for PCT, as reported for Ziylan and Ince (2011), high concentration episodes in different effluents (0.08–13.8 mg L^{-1}) are also described in the literature (Martínez Bueno et al. 2012).

On the other hand, several studies have demonstrated AOPs capability to degrade PCT from different matrixes; more specifically, ozonation (Andreozzi et al. 2003), radiolysis (Szabó et al. 2003), photolysis and UV/H_2O_2 (Kim et al. 2009), heterogeneous photocatalysis (Yang et al. 2008), and Fenton and related process (Trovó et al. 2008; Santos-Juanes et al. 2011a and 2011b; Durán et al. 2011; De Luna et al. 2012; Li et al. 2012). The last processes have been used to degrade this EC at a wide range of concentrations (from 1×10^{-3} to 25 mM). These investigations have confirmed that sole UV irradiation above 254 nm does not degrade PCT or mineralize samples, but the presence of H_2O_2 may lead to total degradation and partial mineralization of the samples (Kim et al. 2009; Trovó et al. 2008; Yang et al. 2008).

Photo-Fenton process, one of the most investigated AOPs for treating PCT, consists in the generation of $HO^\bullet$ by the reaction between H_2O_2 and a Fe(II) salt in acidic medium, under natural or artificial irradiation. The rate of hydroxyl radicals generation in the photo-Fenton process depends on several variables, but reagent doses (H_2O_2 and Fe(II) initial concentrations), irradiation power, and wavelength have demonstrated to be of particular significance (Pignatello et al. 2006).

New process control and modeling approaches have been presented (Cabrera-Reina et al. 2012; Ortega-Gómez et al. 2012), but a more complete understanding of the process will be provided when a model considering photo-enhancement of the process is clarified. As a first step toward this direction, photonic efficiency of PCT degradation via photo-Fenton has to be estimated. Photonic efficiency (Cabrera et al. 1994 and Serpone 1997) provides a more complete representation of photochemical processes and has been employed in recent studies on photo-Fenton pollutant degradation in water (Benzaquén et al. 2012).

Materials and methods

The experiments were performed by treating PCT water solutions in a pilot plant, and process performance was monitored by measuring the concentration of PCT and total organic carbon (TOC) at given time intervals.

Materials

98 % purity PCT by Aldrich was purchased to prepare samples in distilled water. Fenton reagents: H_2O_2 33 % w/v (Panreac) and $Fe_2SO_4\cdot7H_2O$ (Merck) were used as received. Initial pH was set at 3.0±0.1 by adding HCl 37 % (J.T. Baker). Initial pH was set at 3.0±0.1 by adding HCl 37 % (J.T. Baker). Chloride may cause $HO^\bullet$ scavenging, but at pH 2.8 it is reported to be noticeable only above 0.01 M Cl^{-1} (Pignatello

et al. 2006). HPLC gradient grade methanol (J.T. Baker) and filtered milli Q grade water were used as HPLC mobile phases.

Pilot plant

The photochemical pilot plant consists in a 15-L system (Fig. 1a): glass reservoir, annular photo-reactor, and a pumping system set to keep a constant recirculation flow of 12 L min^{-1}, which guarantees perfect mixing. In all the experiments, temperature was monitored to remain within the range 28±2ºC.

Table 1 and Fig. 1b present the characteristics of the annular photo-reactor, which consists two borosilicate cylinders concentrically arranged with an Actinic BL TL-DK 36 W/10 1SL lamp inside. The photo-reactor is connected to the Pyrex reservoir and to a monitoring system. The incident photon flux ($I=q_w A_w$) was measured by potassium ferrioxalate actinometry (Murov 1993), and it was determined to be 3.356×10^{-4} Einstein min^{-1}.

Analytical methods

Total organic carbon (TOC) concentration was measured at regular time intervals of 15 min by means of a Shimadzu $V_{CHS/CSN}$ TOC analyzer.

PCT concentration was determined via HPLC, using an Agilent 1200 series with UV-DAD array detector. Stationary phase was an Akady 5 μm C-18 150×4.6 mm column, maintained at 25 °C, and the diode array detector was set at 243 nm. Mobile phase was a mixture of methanol:water (25:75) flowing at 0.4 mL min^{-1}, and 20-μL samples were injected by a manual injector. Under these conditions, retention time was 8.6 min. A nine-level calibration curve (range 0–50 mg L^{-1}) was used for contaminant quantification. Before injection, samples were treated with 0.1 M sodium sulfite and methanol (in proportion 50:10:40) to stop reaction and prevent further degradation of PCT. This concentration was measured at 1.5, 2.5, 5, 7.5, and 10 min treatment.

H_2O_2 concentration was followed by a spectrophotometric technique described by Nogueira et al. (2005), measuring the absorption at 450 nm of the complex formed after reaction with ammonium metavanadate.

Preliminary Assays

Selection of the reagent doses

A wide range of PCT concentrations have been investigated so far; more specifically, concentrations ranging from 1×10^{-3} to 25 mM have been addressed in the literature. The concentration selected for this study was 40 mg L^{-1} (2.65×10^{-4} M), although it is higher than that found in wastewaters and

Fig. 1 Pilot plant. **a** Schematic representation. **b** Details of the annular photo-reactor
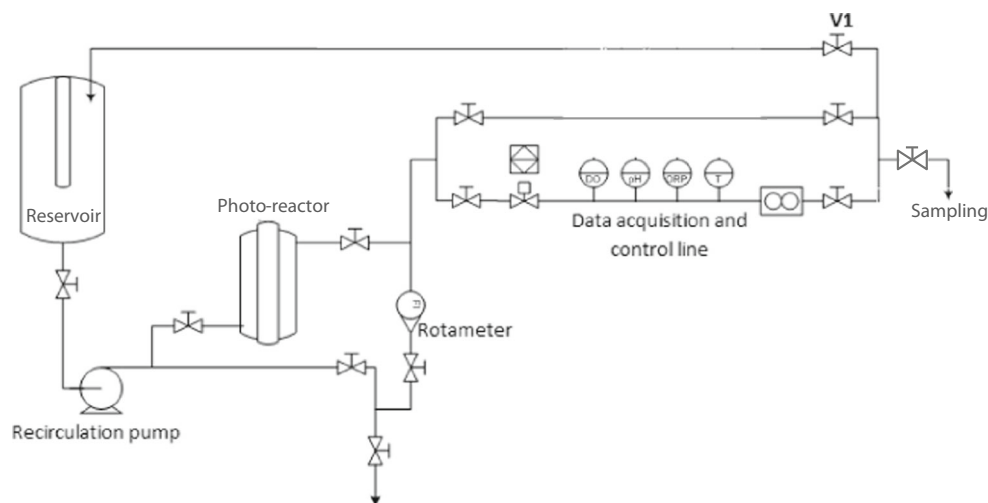

(a)
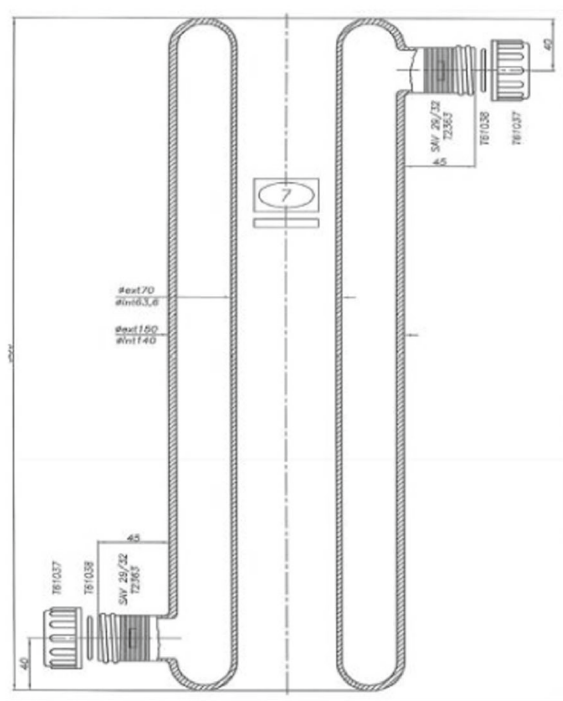
(b)

Table 1 Description of the experimental setup

Annular irradiated height, mm		130.0
Outer cylinder	Outer diameter, mm	150.0
	Inner diameter, mm	140.0
Inner cylinder	Outer diameter, mm	70.0
	Inner diameter, mm	63.6
Total system volume, L		15.0
Annular irradiated volume, L		1.5

groundwater (between 0.05 and 1.9 mg L^{-1} according to Lapworth et al. 2012). This concentration simplifies the monitoring of the concentrations (contaminant and TOC) along the treatment span and is consistent with the detection limit of the available measurement equipment. (0.61 and 2.98 mg L^{-1}, respectively).

Regarding Fe(II) concentration, a maximum level of 10 mg L^{-1} was selected, since it is the maximum legal value in wastewaters in Spain (DOGC). A minimum value of half that maximum (5 mg L^{-1}) was also considered in this study. With regards to H_2O_2 concentration, a stoichiometric dose of

189 mg L^{-1} was used as a reference to achieve total mineralization to CO_2, H_2O and inorganic ions (considering H_2O_2 as the only oxidant in the media, Eq. 1). A range between half and four times such stoichiometric dose (94.5 and 756 mg L^{-1}, respectively) was selected to study the influence of H_2O_2.

$$C_8H_9NO_2 + 21H_2O_2 \rightarrow 8CO_2 + 25H_2O + H^+ + NO_3^- \quad (1)$$
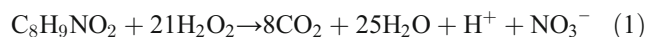
Mixing characterization

Once the concentrations of the reagents was established, it was necessary to guarantee perfect mixing conditions at the most extreme set of operational conditions (40 mg L^{-1} PCT, 10 mg L^{-1} Fe(II), and 756 mg L^{-1} H_2O_2). For that aim, a set of experiments was performed at different recirculation flows, and TOC, PCT, and H_2O_2 concentration were determined. Results show a perfectly agitated system from a recirculation flow of 7.7 L min^{-1}, and a value of 12 L min^{-1} was selected for the subsequent study.

Blank assays

A set of blank assays was performed in order to identify the effect of each reagent on the degradation and mineralization of PCT. The three blank assays undertaken correspond to only irradiation, only Fe(II) at a concentration of 10 mg L^{-1} and only H_2O_2 at a concentration of 756 mg L^{-1}. Results demonstrate that the reagents alone produce no PCT degradation, except in the case of H_2O_2 alone, which led to only 18 % degradation after 90 min treatment. Certainly, sole irradiation could not be expected to degrade PCT as it does not absorb energy in the range of lamp emission.

PCT degradation and mineralization performance

Three factors were considered to characterize the degradation and mineralization of PCT solutions: Fe(II) concentration, H_2O_2 concentration, and presence/absence of irradiation. Hence, the design of experiments presented in Table 2 was undertaken. Samples were withdrawn at regular time intervals and TOC and PCT concentrations were measured.

Figures 2 and 3 show respectively the evolution of PCT and TOC concentrations obtained with 5 and 10 mg L^{-1} Fe(II) initial concentrations at the beginning of the experiment. In both cases, Fenton and photo-Fenton processes are compared for different initial H_2O_2 concentrations.

Figure 3a, b demonstrates that, as it was expected, the presence of irradiation remarkably increases mineralization. In the absence of irradiation, mineralization levels between 28 and 38 % are obtained for both Fe(II) loads after 75 min of reaction.

When irradiation is present, the improvement in mineralization ranges between 15 and 60 percentage points for both Fe(II) concentrations, being higher when higher H_2O_2 loads are used. A 48 % TOC reduction is achieved in the worst case (5 mgL^{-1} Fe(II) and 94.5 mg L^{-1} H_2O_2) after 75 min of reaction. The best results are obtained with 10 mg L^{-1} Fe(II) and 756 mg L^{-1} H_2O_2 initial concentrations, which produces 92 % mineralization in 75 min of operation.

Photonic efficiency

One of the terms used to evaluate the efficiency of a photochemical process is the quantum yield, defined as "the number of molecules which react according to this process divided by the numbers of photons absorbed by the system during the same time" (Braun et al. 1991). In the same way that chemical yield of a reaction measures the usage of a given reagent to produce a desired product, the quantum yield measures the usage of photons to produce the desired product in a photochemical reaction. Furthermore, complex phenomenological models, considering the local volumetric rate of photon absorption (LVRPA, Cassano et al. 1995) require the determination of such term to provide more applicable and flexible modeling options.

Another term is the photonic efficiency or apparent quantum efficiency, which is simple to compute and useful for polychromatic radiation. It is defined by Benzaquén et al. (2012) as "the ratio of the number of reactant molecules degraded during a given time, to the total number of photons arrived at the reactor wall, during the same period of time". Mathematically, it can be expressed for a generic reagent "A" as follows:

$$\varphi_{pho,A} = \frac{[\text{amount of } A \text{ molecules converted at time } t]}{[\text{amount of photons supplied to the reactor at time } t]} \quad (2)$$

Applying the previous concept to PCT degradation, photonic efficiency can be calculated as:

$$\varphi_{pho,PCT} = \frac{\left(C_{t_0}^{PCT} - C_{t_f}^{PCT}\right)V_T}{q_w A_w \left(t_f - t_0\right)} \quad (3)$$

where $\phi_{pho,PCT}$ is the photonic efficiency of PCT degradation (mol Einstein^{-1}), $C_{t_0}^{PCT}$ and $C_{t_f}^{PCT}$ are PCT concentrations at initial and final time (t_0 and t_f), respectively, (mol L^{-1}), V_T the total volume of reaction (L), q_w the spectral net radiation flux at the reactor wall (Einstein cm^{-2} s^{-1}) and A_w the irradiated area (cm^2).

Table 2 Design of experiments for the characterization of PCT degradation

C^{PCT} (mg L^{-1})	$C^{Fe(II)}$ (mg L^{-1})	C^{H2O2} (mg L^{-1})	Irradiation	Experiment code
40	5	94.5	ON	PCT_40_5_94.5_ON
			OFF	PCT_40_5_94.5_OFF
		189	ON	PCT_40_5_189_ON
			OFF	PCT_40_5_189_OFF
		378	ON	PCT_40_5_378_ON
			OFF	PCT_40_5_378_OFF
		756	ON	PCT_40_5_756_ON
			OFF	PCT_40_5_756_OFF
	10	94.5	ON	PCT_40_10_94.5_ON
			OFF	PCT_40_10_94.5_OFF
		189	ON	PCT_40_10_189_ON
			OFF	PCT_40_10_189_OFF
		378	ON	PCT_40_10_378_ON
			OFF	PCT_40_10_378_OFF
		756	ON	PCT_40_10_756_ON
			OFF	PCT_40_10_756_OFF
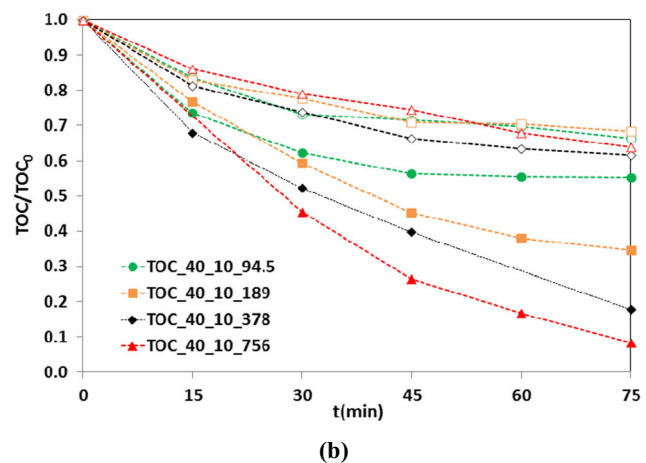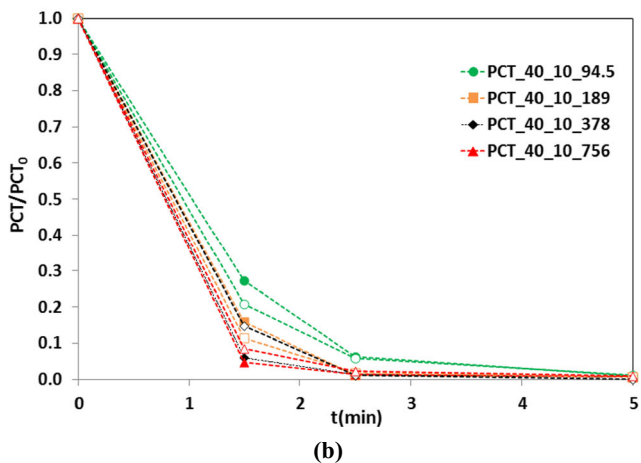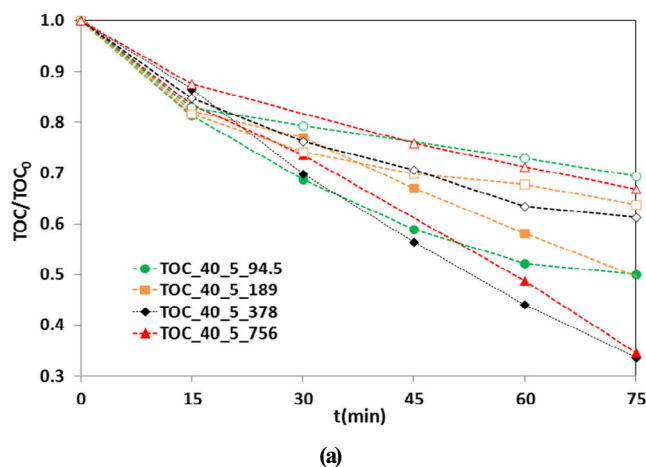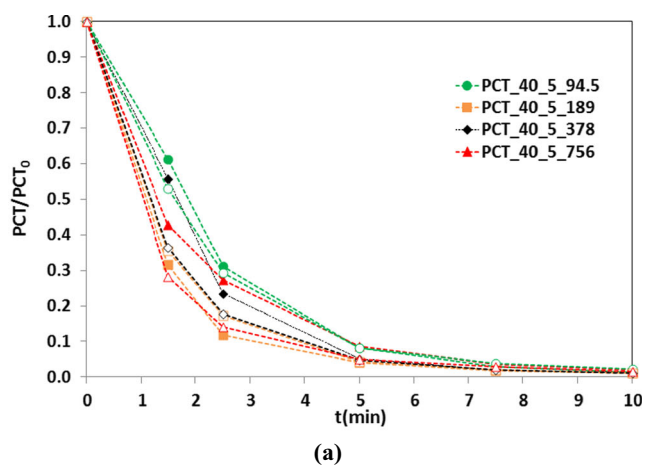
Fig. 2 Evolution of PCT concentration for Fenton (*void symbols*) and photo-Fenton (*solid symbols*) processes. **a** 5 mg L^{-1} Fe(II). **b** 10 mg L^{-1} Fe(II)

Fig. 3 Evolution of TOC concentrations for Fenton (*void symbols*) and photo-Fenton (*solid symbols*) processes. **a** 5 mg L^{-1} Fe(II). **b** 10 mg L^{-1} Fe(II)
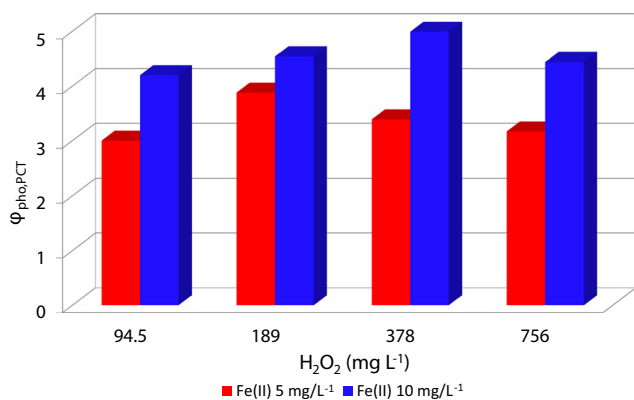
Fig. 4 Photonic efficiency for PCT degradation at 2.5 min treatment as a function of H_2O_2 concentration for two Fe(II) initial concentration (*blue* 10 mg L^{-1}. *Red* 5 mg L^{-1})

In a similar way, the photonic efficiency of mineralization (TOC reduction), $\phi_{pho,TOC}$, can be expressed as:

$$\varphi_{pho,TOC} = \frac{\left(C_{t_0}^{TOC} - C_{t_f}^{TOC}\right) V_T}{q_w A_w \left(t_f - t_0\right)} \quad (4)$$

In this study, the influence of the concentration of H_2O_2 for both on photonic efficiency of PCT degradation and mineralization (TOC) was determined in order to identify the best operational conditions which improve the usage of the irradiation. Results are presented in further sub-sections.

Photonic efficiency of PCT degradation ($\phi_{pho,PCT}$)

Photonic efficiency of degradation was calculated at different H_2O_2 concentrations. Figure 4 presents the results for a reaction time of 2.5 min. First, note that for all H_2O_2 concentrations evaluated, the photonic efficiencies for 10 mg L^{-1} of
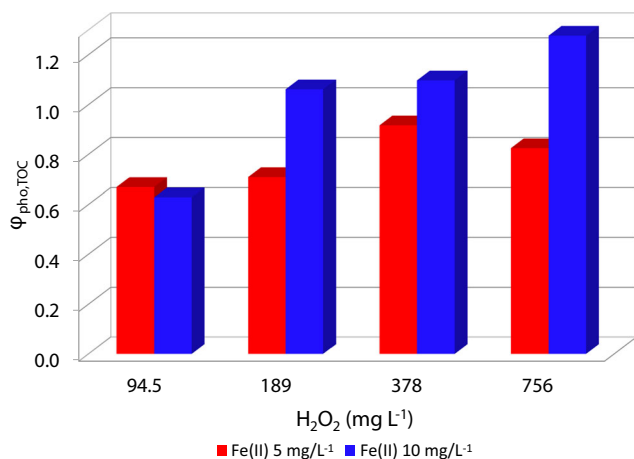
Fig. 5 Photonic efficiency for TOC degradation at 75 min treatment as a function of H_2O_2 concentration for two Fe(II) initial concentration (*blue* 10 mg L^{-1}. *Red* 5 mg L^{-1})
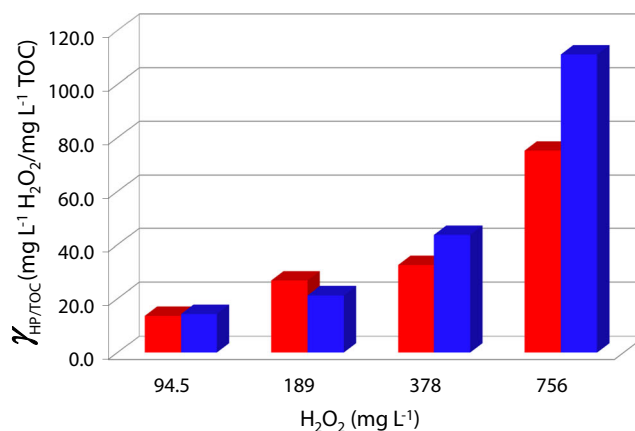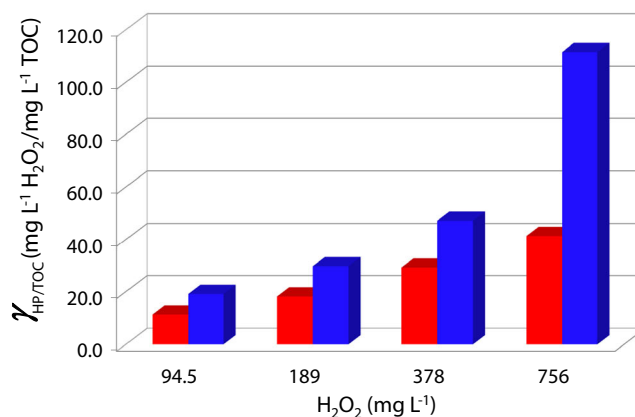
Fig. 6 Specific consumption of the oxidizing agent at 15 min treatment as a function of H_2O_2 concentration for two Fe(II) initial concentration. **a** Fe(II) 5 mg L^{-1}; **b** Fe(II) 10 mg L^{-1}. (*Blue* Fenton. *Red* photo-Fenton)

Fe(II) are higher than the corresponding for 5 mg L^{-1} of Fe(II). Besides, the beneficial effect of increasing the Fe(II) concentration (between the ranges of legal value in wastewaters in Spain (DOGC)) can be observed. It should be noted that these results are consistent with the differences in the degradation rate observed in Fig. 2a, b.

For conditions of Fe(II) 10 mg L^{-1}, the maximum degradation efficiencies are the ones obtained for 378 mg L^{-1} of H_2O_2 ($\phi_{pho,PCT}$=5). In addition, an increase in degradation efficiencies can be observed when increasing the value of H_2O_2 for the range 94.5–378 mg L^{-1}. However, for high concentrations of H_2O_2 (756 mg L^{-1}), the conversion of PCT is less than for H_2O_2=378 mg L^{-1}, so there is a reduction in photonic efficiencies. Note that for high concentrations, H_2O_2 acts as a "scavenger" radical, competing in pollutant degradation and reducing the reaction rate.

Similar behavior is observed for the system using 5 mg L^{-1} of Fe(II). However, an increase in degradation efficiencies with increasing the value of H_2O_2 only for the range 94.5–189 mg L^{-1} was observed. For this Fe(II) concentration, the

maximum degradation efficiencies are the ones obtained for H_2O_2 189 mg L^{-1} ($\phi_{pho,PCT}$=3.9).

Photonic efficiency of mineralization ($\phi_{pho,TOC}$)

Figure 5 presents the photonic efficiency of mineralization at different H_2O_2 concentrations for 75 min of reaction. First, it is worth noting that for all H_2O_2 concentrations evaluated, these mineralization efficiencies are lower than the corresponding PCT degradation efficiencies. This was expected, as PCT degradation is much faster than mineralization (see Figs. 2 and 3). For 5 mg L^{-1} Fe(II), the maximum mineralization efficiency ($\phi_{pho,TOC}$=0.92) was obtained for 378 mg L^{-1} H_2O_2. Whereas for 10 mg L^{-1} Fe (II), this maximum ($\phi_{pho,TOC}$=1.28) was reached to 756 mg L^{-1} H_2O_2. These concentrations of H_2O_2 are not in agreement with those obtained for degradation efficiencies. Note that this mineralization involves the degradation of all the organic matter in the sample. However, the beneficial effect of increasing the Fe(II) concentration can be observed again.

Oxidizing agent consumption

For the mineralization process, it is important to assess simultaneously the consumption of the oxidizing agent. Therefore, a useful parameter to evaluate the H_2O_2 consumption for this process is the "specific consumption of the oxidizing agent" ($\gamma_{HP/TOC}$), defined as

$$\gamma_{HP/TOC} = \frac{\left(C_{t_0}^{HP}-C_{t_f}^{HP}\right)}{\left(C_{t_0}^{TOC}-C_{t_f}^{TOC}\right)} \tag{5}$$

A multiple bar chart can be employed to show the effects of irradiation in the values of $\gamma_{HP/TOC}$ for all H_2O_2 concentrations (Fig. 6).

It should be noted that, for all operating conditions of H_2O_2 and both Fe(II) concentration, the $\gamma_{HP/TOC}$ values obtained for Fenton process were always higher than the corresponding values observed for photo-Fenton (except only for conditions of Fe(II) 5 mg L^{-1} and 189 mg L^{-1} H_2O_2). This implies a less efficient use of the oxidizing agent for dark conditions. Furthermore, these differences for each H_2O_2 concentration evaluated were increased for 10 mg L^{-1} of Fe(II), reaching a maximum at H_2O_2 756 mg L^{-1}. Again the beneficial effect of increasing the Fe(II) concentration can be observed.

Conclusions

Photonic efficiencies for the photo-Fenton PCT degradation and mineralization were evaluated in an annular photo-reactor operating in perfect mixing conditions. The influence of H_2O_2 and Fe(II) concentrations on the pollutant degradation and mineralization process was determined.

For all the operation conditions evaluated, PCT degradation is efficiently attained by both Fenton and photo-Fenton processes. The presence of irradiation was confirmed to remarkably improve mineralization of PCT samples by Fenton process, providing until 60 % more mineralization than thermal Fenton process when 10 mg L^{-1} Fe(II) are loaded. It is worth mentioning that Fe(II) loads inside the legal limit (10 mg L^{-1}) are enough to guaranty even 92 % TOC reduction, while half that dose leads only to 65 % mineralization in the same conditions.

The maximum photonic degradation efficiencies for 5 and 10 mg L^{-1} Fe(II) were found to be 3.9 (H_2O_2=189 mg L^{-1}) and 5 (H_2O_2=378 mg L^{-1}), respectively. For higher concentrations of oxidant, H_2O_2 acts as a "scavenger" radical, competing in pollutant degradation and reducing the reaction rate.

For all H_2O_2 concentrations evaluated, the mineralization photonic efficiencies are lower than the corresponding PCT degradation efficiencies. This was expected, as PCT degradation is much faster than mineralization. For 5 mg L^{-1} Fe(II) the maximum mineralization efficiency ($\phi_{pho,TOC}$=0.92) was obtained for 378 mg L^{-1} H_2O_2. Whereas for 10 mg L^{-1} Fe (II), this maximum ($\phi_{pho,TOC}$=1.28) was reached for 756 mg L^{-1} H_2O_2. The effect of increasing the Fe(II) concentration can be also observed.

The consumption of the oxidizing agent during the Fenton and photo-Fenton treatment was also evaluated. For all operating conditions of H_2O_2 and both Fe(II) concentrations, the values of specific consumption of the oxidant agent obtained for Fenton process were always higher than the corresponding values observed for photo-Fenton system.

Hence, the characterization of paracetamol degradation produced by this experimental work allows research on further assessment of the radiation field and modeling of the process, which is currently underway.

References

Andreozzi R, Caprio V, Marotta R, Vogna D (2003) Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system. Water Res 37:993–1004

Becerril K (2009) Emerging contaminants in water. Digital Journal 10(8) http://www.revista.unam.mx/vol.10/num8/ art54/art54.pdf. Accessed 24 June 2012

Benzaquén TB, Isla MA, Alfano OM (2012) Quantum efficiencies of the photo-Fenton degradation of atrazine in water. Water Sci Technol 66:2209–2216

Braun AM, Maurette M-T, Oliveros E (1991) Photochemical technology. Wiley, London

Broséus R, Vincent S, Aboulfadl K, Daneshvar A, Sauvé S, Barbeau B, Prévost M (2009) Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. Water Res 43:4707–4717

Cabrera MI, Alfano OM, Cassano AE (1994) Novel reactor for photo-catalytic kinetic studies. Ind Eng Chem Res 33(12):3031–3042

Cabrera Reina A, Santos-Juanes L, García JL, Casas JL, Sánchez JS (2012) Modelling photo-Fenton process for organic matter mineralization, hydrogen peroxide consumption and dissolved oxygen evolution. Appl Catal B 119–120:132–138

Cassano AE, Martin CA, Brandi Rodolfo J, Orlando OM (1995) Photoreactor analysis and design: fundamentals and applications. Ind Eng Chem Res 34:2155–2201

De Luna MDG, Veciana ML, Su C-C, Lu M-C (2012) Acetaminophen degradation by electro-Fenton and photoelectro-Fenton using a double cathode electrochemical cell. J Hazard Mater 217–218:200–207

DOGC núm. 3894, DECRET 130/2003, de 13/05/2003, (29.5.2003). (URL: http://www.gencat.cat/diari/3894/03127147.htm, accessed 16/07/2013)

Durán A, Monteagudo JM, Carnicer A, Ruiz-Murillo M (2011) Photo-Fenton mineralization of synthetic municipal wastewater effluent containing acetaminophen in a pilot plant. Desalination 270:124–129

Gültekin I, Ince N (2007) Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes. J Environ Manag 85:816–832

Kim I, Yamashita N, Tanaka H (2009) Photodegradation of pharmaceuticals and personal care products during UV and UV/H_2O_2 treatments. Chemosphere 77:518–525

Lapworth DJ, Baran N, Stuart ME, Ward RS (2012) Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ Pollut 163:287–303

Li W, Nanaboina V, Zhou Q, Korshin GV (2012) Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products. Water Res 46:403–412

Martínez Bueno MJ, Gomez MJ, Herrera S, Hernando MD, Agüera A, Fernández-Alba AR (2012) Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: two years pilot survey monitoring. Environ Pollut 164:267–273

Murov SL (1993) Handbook of photochemistry. Dekker, New York

Nogueira RFP, Oliveira MC, Paterlini WC (2005) Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate. Talanta 66:86–91

Ortega-Gómez E, Moreno Úbeda JC, Álvarez Hervás JD, Casas López JL, Santos-Juanes Jordá L, Sánchez Pérez JA (2012) Automatic dosage of hydrogen peroxide in solar photo-Fenton plants: development of a control strategy for efficiency enhancement. J Hazards Mater 237–238:223–230

Petróvic M, González S, Barceló D (2003) Analysis and removal of emerging contaminants in wastewater and drinking water. TrAC Trends Anal Chem 22(10):685–696

Pignatello JJ, 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):1–84

Santos-Juanes Jorda L, Ballesteros Martín MM, Ortega Gómez E, Cabrera Reina A, Román Sánchez IM, Casas López JL, Sánchez Pérez JA (2011) Economic evaluation of the photo-Fenton process. Mineralization level and reaction time: the keys for increasing plant efficiency. J Hazard Mater 186:1924–1929

Santos-Juanes L, García Sánchez JL, Casas López JL, Oller I, Malato S, Sánchez Pérez JA (2011) Dissolved oxygen concentration: a key parameter in monitoring the photo-Fenton process. Appl Catal B 104:316–323

Serpone N (1997) Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. J Photochem Photobiol A 104(1–3):1–12

Szabó L, Tóth T, Homloka R, Takács E, Wojnárovits L (2003) Radiolysis of paracetamol in dilute aqueous solution. Radiat Phys Chem 66(2):137–143

Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. Water Res 32:3245–3260

Trovó AG, Santos Melo SA, Nogueira RFP (2008) Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process—application to sewage treatment plant effluent. J Photochem Photobiol A 198:215–220

Yang L, Yu LE, Ray MB (2008) Degradation of paracetamol in aqueous solutions by TiO_2 photocatalysis. Water Res 42:3480–3488

Ziylan A, Ince NH (2011) The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: treatability by conventional and non-conventional processes. J Hazard Mater 187(1–3):24–36