Photonic Efficiency of the Photodegradation of Paracetamol in Water by the Photo-Fenton Process

E. Yamal-Turbay[1]*, E. Ortega[1], L.O. Conte[3], M. Graells[1], H.D. Mansilla[2], O.M. Alfano[3], M. Pérez-Moya[1].

(1) Escola Universitària d'Enginyeria Tècnica Industrial de Barcelona, c/Comte d'Urgell 187, 08036 Barcelona

(2) Facultad de Ciencias Químicas, Universidad de Concepción, Chile

(3) INTEC, Universidad Nacional del Litoral and CONICET, Santa Fe, Argentina

Abstract

An experimental study of the homogeneous Fenton and photo-Fenton degradation of 4-amidophenol (PCT) is presented. For all the operation conditions evaluated, PCT degradation is efficiently attained by both Fenton and photo-Fenton processes in less than 10 min reaction time. Also, photonic degradation and mineralization efficiencies are determined under different experimental conditions, identifying the influence of the hydrogen peroxide and iron(II) on both contaminant degradation and sample mineralization. The maximum photonic degradation efficiencies for 5 and 10 ppm Fe(II) being 3.9 (HP=189 ppm) and 5 (HP=378 ppm), respectively. For higher concentrations of oxidant, hydrogen peroxide 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 HP and both iron concentration, the consumption values obtained for Fenton process were always higher than to the corresponding values observed for photo-Fenton. This implies a less efficient use of the oxidizing agent for dark conditions

Keywords: Photonic efficiency, paracetamol degradation, Specific Consumption of the Hydrogen Peroxide, photo-Fenton, emerging contaminants.

1. Introduction

Emerging contaminants (ECs) have been receiving increasing attention during the last decades and a lot of efforts have 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,

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* Corresponding author: Evelyn Yamal Turbay. e-mail: evelyn.yamal@gmail.com

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$^\bullet$), 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 the last years (Martínez Bueno et al. 2012). It has been found in European Sewage Treatment Plants in concentrations around 6 µg L^{-1} (Ternes 1998) and 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) have been used to degrade this EC at a wide range of concentrations (from 5x10^{-6} 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 hydrogen peroxide 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 hydrogen peroxide and an 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; Carra 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 in order to provide a more complete representation of the process.

2. 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.

2.1. Materials

98% purity PCT by Aldrich was purchased to prepare samples in distilled water. Fenton reagents: H_2O_2 33% w/v (Panreac) and $Fe_2SO_4 \cdot 7H_2O$ (Merck) were used as received. Initial pH was set at 3.0±0.1 by adding HCl 37% (J.T. Baker). HPLC gradient grade methanol (J.T. Baker) and filtered milli Q grade water were used as HPLC mobile phases.

2.2. Pilot plat

The photochemical pilot plant consists in a 15 L system (Fig. 1): 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 of the experiments temperature was kept at 28±2°C.
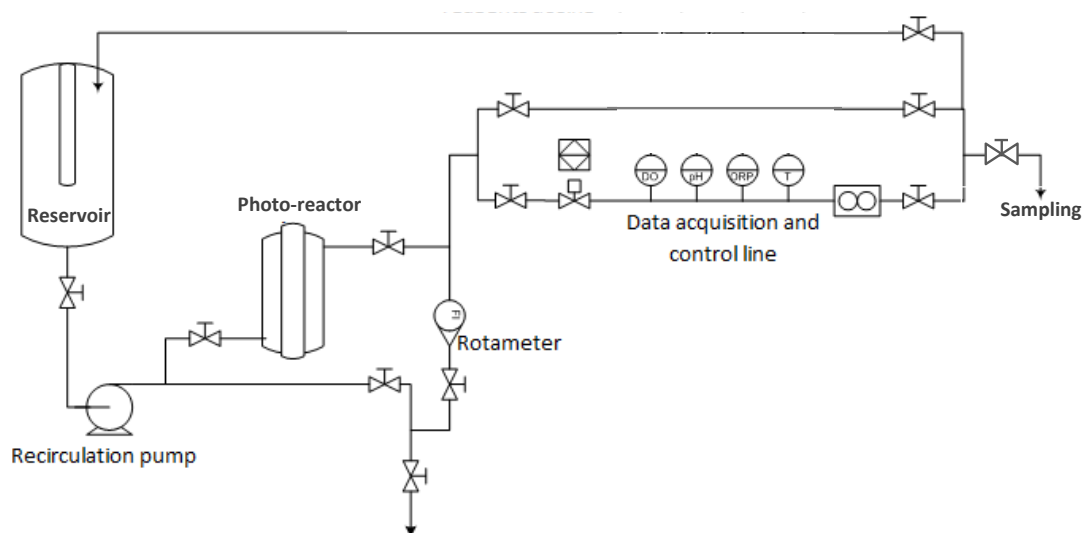

Fig. 1 Pilot plant schematic representation

Table 1 presents the characteristics of the annular photo-reactor, which consists of two concentrically arranged cylinders (an outer one made of Pyrex and an inner one made of quartz with an Actinic BL TL-

DK 36W/10 1SL lamp inside of it) and it is linked 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}.

Table 1 Description of the cylindrical photo-reactor

Height, mm		500
Outer cylinder	Outer diameter, mm	150
	Inner diameter, mm	140
Inner cylinder	Outer diameter, mm	70
	Inner diameter, mm	63.6
Measured volume (approx.), L		5.77

2.3. Analytical methods

Total organic carbon (TOC) concentration was measured at regular time intervals of 15 minutes 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 150x4.6 mm column, maintained at 25ºC 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 minutes. A nine-level calibration curve (range 0-50 mg L^{-1}) was used for contaminant quantification. Before injection, samples were treated with 0.1M sodium sulfite and methanol (in proportion 50:10:40) to stop reaction and prevent further degradation of PCT and its intermediates. This concentration was measured at 1.5, 2.5, 5, 7.5 and 10 minutes treatment.

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

3. Preliminary Assays

3.1. 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 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, TOC, and possible intermediates) along the treatment span and is consistent with the detection limit of the available measurement equipment.

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 (HP) 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 HP 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 HP.

$$C_8H_9NO_2 + 21H_2O_2 \rightarrow 8CO_2 + 25H_2O + H^+ + NO_3^- \tag{1}$$
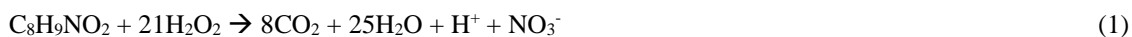
3.2. Mixing characterization

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} HP). For that aim, a set of experiments was performed at different recirculation flows, and TOC, PCT and HP 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.

3.3. 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 HP at a concentration of 756 mg L^{-1}. Results demonstrate that the reagents alone produce no PCT degradation, except in the case of HP alone, which led to only 18% degradation after 90 minutes treatment. Certainly, sole irradiation could not be expected to degrade PCT as it does not absorb energy in the range of lamp emission.

4. PCT Degradation and Mineralization Performance

Three factors were considered to characterize the degradation and mineralization of PCT solutions: Fe(II) concentration, HP 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.

Table 2 Design of experiments for the characterization of PCT degradation

C^{PCT} (mg L^{-1})	$C^{Fe(II)}$ (mg L^{-1})	C^{HP} (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

Figures 2 and 3 show respectively the evolution of PCT and TOC concentrations obtained with 5 mg L^{-1} 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 HP concentrations.
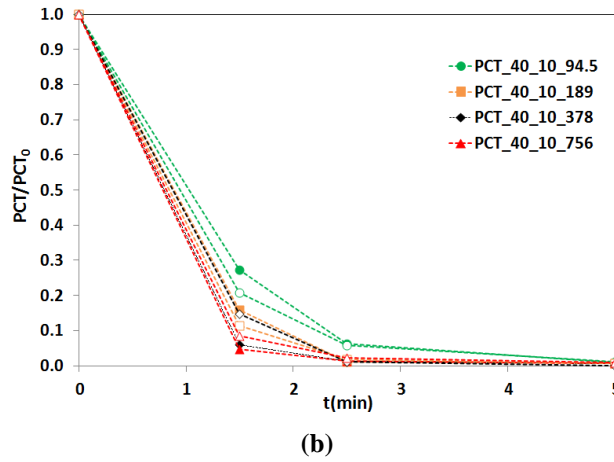

(a)

(b)
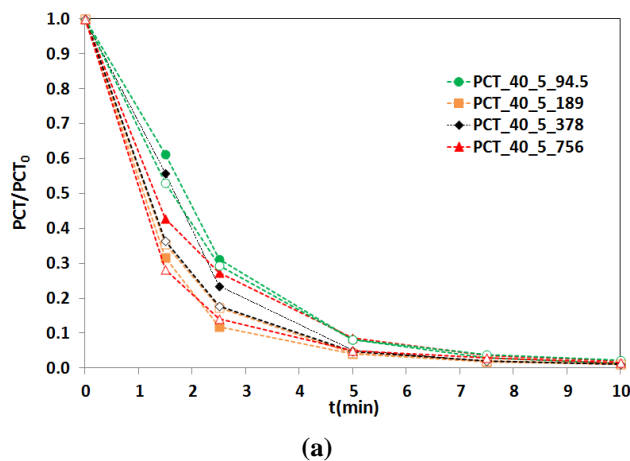
Fig. 2 Evolution of PCT concentration for Fenton (void symbols) and photo-Fenton (solid symbols)

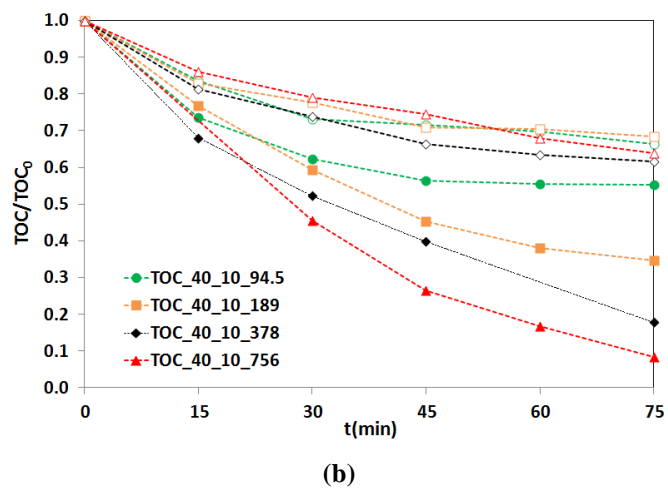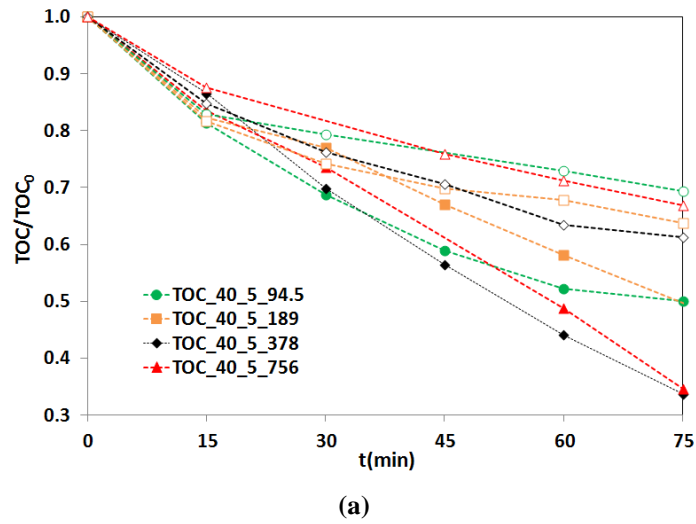processes **(a)** 5 mg L^{-1} Fe(II) **(b)** 10 mg L^{-1} Fe(II)

(a)

(b)

Fig. 3 Evolution of TOC concentrations for Fenton (void symbols) and photo-Fenton (solid symbols)

processes **(a)** 5mg L^{-1} Fe(II) **(b)** 10mg L^{-1} Fe(II)

Figures 3(a) and (b) demonstrate 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 a 60 percentage points for both Fe(II) concentrations, being higher when higher HP loads are used. A 48% TOC reduction is achieved in the worst case (5 mgL^{-1} Fe(II) and 94.5 mg L^{-1} HP) 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 minutes of operation.

5. 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:

$$\phi_{pho,A} = \frac{[amount \ of \ A \ molecules \ converted \ at \ time \ t]}{[amount \ of \ photons \ supplied \ to \ the \ reactor \ at \ time \ t]} \tag{2}$$

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

$$\phi_{pho,PCT} = \frac{(C_{t_0}^{PCT} - C_{t_f}^{PCT})V_T}{q_w A_w (t_f - t_0)} \tag{3}$$

where $\phi_{pho,PCT}$ is the photonic efficiency of PCT degradation (mol/Einstein), $C_{t_0}^{PCT}$ and C_{tf}^{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).

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

$$\phi_{pho,TOC} = \frac{(C_{t_0}^{TOC} - C_{t_f}^{TOC})V_T}{q_w A_w (t_f - t_0)} \tag{4.4}$$

In this study, the influence of the concentration of HP 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.

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

Photonic efficiency of degradation was calculated at different HP concentrations. Fig. 4 presents the results for a reaction time of 2.5 min. First note that for all HP concentrations evaluated, the photonic efficiencies for 10 ppm of Fe(II) are higher than the corresponding for 5 ppm of Fe(II). Besides, the beneficial effect of increasing the iron 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. 2(a) and (b).
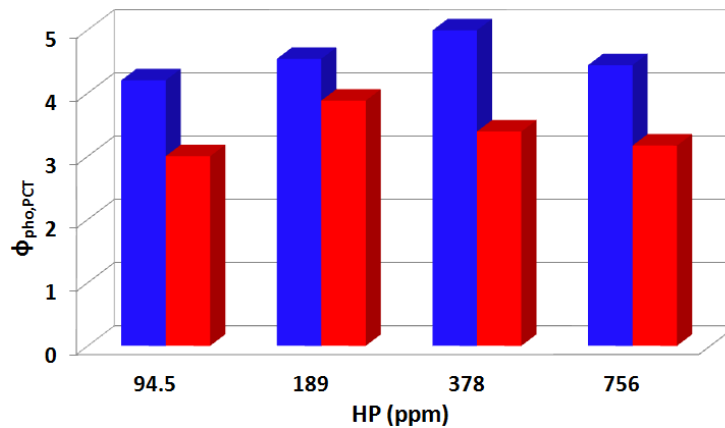

Fig. 4 Photonic efficiency for PCT degradation at 2.5 min treatment as a function of HP concentration for two Fe(II) initial concentration (Blue: 10 mg L^{-1}. Red: 5 mg L^{-1})

For conditions of Fe(II) 10 ppm the maximum degradation efficiencies being the one obtained for 378 ppm of HP ($\phi_{pho,PCT}$ = 5). In addition, one can observe an increase in degradations efficiencies with increasing the value of HP for the range 94.5-378 ppm. However, for high concentrations of hydrogen peroxide (HP = 756 ppm), the conversion of PCT is less than for HP = 378 ppm, so there is a reduction in photonic efficiencies. Note that for high concentrations, hydrogen peroxide acts as a "scavenger" radical, competing in pollutant degradation and reducing the reaction rate.

Similar behavior is observed for the system using 5 ppm of iron. However, an increase in degradations efficiencies with increasing the value of HP only for the range 94.5-189 ppm was observed. For this iron concentration the maximum degradation efficiencies being the one obtained for HP 189 ppm ($\phi_{pho,PCT}$ = 3.9).

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

Figure 5 presents the photonic efficiency of mineralization at different HP concentrations for 75 min of reaction. First, note that for all hydrogen peroxide 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 Fig. 2 and 3). For 5 ppm Fe(II) the maximum mineralization efficiency ($\phi_{pho,TOC}$ = 0.92) was obtained for 378 ppm HP. Whereas for 10 ppm Fe (II) this maximum ($\phi_{pho,TOC}$ = 1.28) was reached to 756 ppm HP. These optimal concentrations of hydrogen peroxide 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 iron concentration can be observed again.
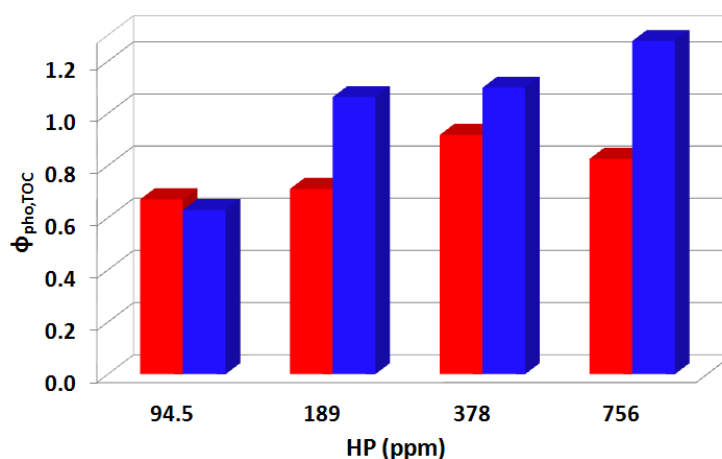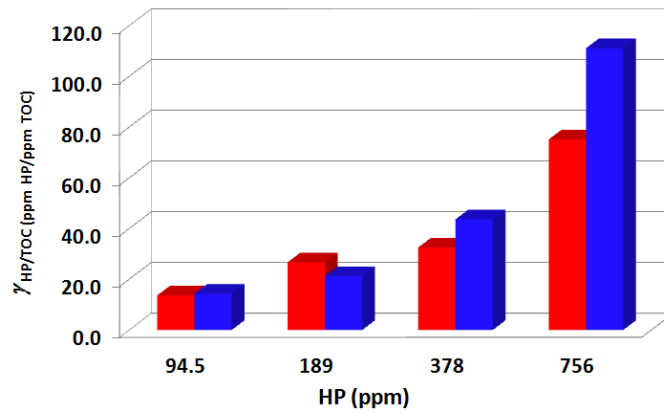
Fig. 5 Photonic efficiency for TOC degradation at 75 min treatment as a function of HP concentration for two Fe(II) initial concentration (Blue: 10 mg L^{-1}. Red: 5 mg L^{-1})
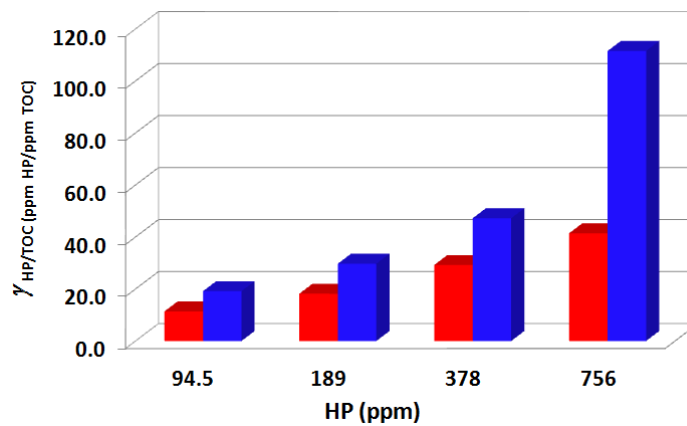
6. Oxidizing agent consumption

For the mineralization process, is important to assess simultaneously the consumption of the oxidizing agent. Therefore, a useful parameter to evaluate the hydrogen peroxide consumption for this process is the "Specific Consumption of the Oxidizing Agent" ($\gamma_{HP/TOC}$), defined as

$$\gamma_{HP/TOC} = \frac{(C_{t_0}^{HP} - C_{t_f}^{HP})}{(C_{t_0}^{TOC} - C_{t_f}^{TOC})} \qquad (4.5)$$

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

(a)

(b)

Fig. 6 Specific Consumption of the Oxidizing Agent at 15 min treatment as a function

of HP concentration for two Fe(II) initial concentration (a) Fe(II) 5 ppm; (b) Fe(II) 10

ppm. (Blue: Fenton. Red: foto-Fenton)

It should be noted that, for all operating conditions of HP and both iron concentration, the $\gamma_{HP/TOC}$ values

obtained for Fenton process were always higher than to the corresponding values observed for photo-

Fenton (except only for conditions of Fe(II) 5 ppm and 189 ppm HP). This implies a less efficient use of

the oxidizing agent for dark conditions. Furthermore, these differences for each HP concentration

evaluated were increased for 10 ppm of iron, reaching a maximum at HP 756 ppm. Again the beneficial

effect of increasing the iron concentration can be observed.

7. 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 hydrogen peroxide and

iron 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 in less than 10 min reaction time. Even more, total PCT degradation is possible

within the first 5 min process when 10 ppm Fe(II) is used.

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 mention, that iron loads inside the legal limit (10 mg•L-1) are enough to

guaranty even 92% TOC reduction within 75 minutes treatment, while half that dose leads to 65 %

mineralization.

The maximum photonic degradation efficiencies for 5 and 10 ppm Fe(II) being 3.9 (HP=189 ppm) and 5

(HP=378 ppm), respectively. For higher concentrations of oxidant, hydrogen peroxide acts as a

"scavenger" radical, competing in pollutant degradation and reducing the reaction rate.

For all HP 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 ppm Fe(II) the maximum mineralization efficiency ($\square$pho,TOC = 0.92) was

obtained for 378 ppm HP. Whereas for 10 ppm Fe (II) this maximum ($\square$pho,TOC = 1.28) was reached

for 756 ppm HP. The effect of increasing the iron 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 HP and both iron 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.

Acknowledgements

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