

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

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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 ($\text{H}_2\text{O}_2 = 189 \text{ mg L}^{-1}$) and 5 ($\text{H}_2\text{O}_2 = 378 \text{ mg L}^{-1}$), 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.

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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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- μ g/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 $6 \mu\text{g L}^{-1}$ (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 1×10^{-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 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 (Benzaquén et al. 2012) 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: H₂O₂ 33% w/v (Panreac) and Fe₂SO₄·7H₂O (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• scavenging, but at pH 2.8 it is reported to be noticeable only above 0.01M Cl⁻¹ (Pignatello et al., 1992). HPLC gradient grade methanol (J.T. Baker) and filtered milli Q grade water were used as HPLC mobile phases.

2.2. 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 of the experiments temperature was kept at 28±2°C.

Table 1 and Fig. 1b present the characteristics of the annular photo-reactor, which consists of two borosilicate cylinders concentrically arranged with an Actinic BL TL-DK 36W/10 1SL lamp inside. The photo-reactor is connected to the Pyrex reservoir and to a monitoring system. The incident photon flux ($I = q_w \cdot A_w$) was measured by potassium ferrioxalate actinometry (Murov 1993) and it was determined to be 3.356x10⁻⁴ Einstein min⁻¹.

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 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 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. This concentration was measured at 1.5, 2.5, 5, 7.5 and 10 minutes treatment.

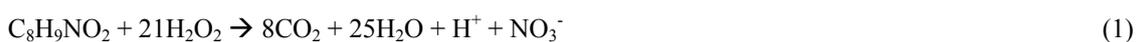
H_2O_2 concentration was followed by a spectrophotometric technique described by Nogueira et al. (2005), measuring the absorption at 450 nm of the complex formed after reaction with ammonium metavanadate.

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 and TOC) along the treatment span and is consistent with the detection limit of the available measurement equipment. (0.61 mg L^{-1} 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 .



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 H₂O₂). For that aim, a set of experiments was performed at different recirculation flows, and TOC, PCT and H₂O₂ 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 H₂O₂ at a concentration of 756 mg L⁻¹. Results demonstrate that the reagents alone produce no PCT degradation, except in the case of H₂O₂ 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, H₂O₂ 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 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 H₂O₂ concentrations.

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 H₂O₂ loads are used. A 48% TOC reduction is achieved in the worst case (5 mgL⁻¹ Fe(II) and 94.5 mg L⁻¹ H₂O₂) after 75 min of reaction. The best results are obtained with 10 mg L⁻¹ Fe(II) and 756 mg L⁻¹ H₂O₂ 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:

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

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

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

where $\phi_{\text{pho},\text{PCT}}$ is the photonic efficiency of PCT degradation (mol Einstein^{-1}), $C_{t_0}^{\text{PCT}}$ and $C_{t_f}^{\text{PCT}}$ 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 ($\text{Einstein cm}^{-2} \text{ s}^{-1}$) and A_w the irradiated area (cm^2).

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

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

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.

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

Photonic efficiency of degradation was calculated at different H_2O_2 concentrations. Fig. 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 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. 2(a) and (b).

For conditions of Fe(II) 10 mg L^{-1} the maximum degradation efficiencies being the one 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 $94.5\text{-}378\text{ mg L}^{-1}$. However, for high concentrations of H_2O_2 (756 mg L^{-1}), the conversion of PCT is less than for $H_2O_2 = 378\text{ mg L}^{-1}$, 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 degradations efficiencies with increasing the value of H_2O_2 only for the range $94.5\text{-}189\text{ mg L}^{-1}$ was observed. For this Fe(II) concentration the maximum degradation efficiencies being the one obtained for $H_2O_2\ 189\text{ mg L}^{-1}$ ($\phi_{pho,PCT} = 3.9$).

5.2. 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 Fig. 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.

6. 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 H₂O₂ consumption for this process is the “Specific Consumption of the Oxidizing Agent” ($\gamma_{HP/TOC}$), defined as

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

A multiple bar chart can be employed to show the effects of irradiation in the values of $\gamma_{HP/TOC}$ for all H₂O₂ concentrations (Figure 6).

It should be noted that, for all operating conditions of H₂O₂ 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 H₂O₂). This implies a less efficient use of the oxidizing agent for dark conditions. Furthermore, these differences for each H₂O₂ concentration evaluated were increased for 10 mg L⁻¹ of Fe(II), reaching a maximum at H₂O₂ 756 mg L⁻¹. Again the beneficial effect of increasing the Fe(II) 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 H₂O₂ 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 mention, 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 (H₂O₂ = 189 mg L⁻¹) and 5 (H₂O₂ = 378 mg L⁻¹), respectively. For higher concentrations of oxidant, H₂O₂ acts as a "scavenger" radical, competing in pollutant degradation and reducing the reaction rate.

For all H₂O₂ 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 H₂O₂. Whereas for 10 mg L⁻¹ Fe (II) this maximum ($\phi_{pho,TOC} = 1.28$) was reached for 756 mg L⁻¹ H₂O₂. 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 H₂O₂ 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.

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