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DEGRADATION OF PARACETAMOL IN AQUEOUS SOLUTION: COMPARISON OF DIFFERENT UV INDUCED ADVANCED OXIDATION PROCESSES

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Abstract— Environmental hazards are a consequence of the massive use of synthetic chemicals that are prevalent in nearly every aspect of modern life. The outburst of the so-called “emerging pollutants” (pharmaceuticals and pesticides among others) generates an additional problem due to the scarce available information on their impact on the environment or their interferences with the biological processes. Among them, paracetamol is one of the drugs the most widely found in hospital effluents, in the effluents of wastewater treatment plants, as well as in rivers. In this work, the feasibility of paracetamol degradation by different processes based on ultraviolet radiation is discussed: photolysis, photo-oxidation with hydrogen peroxide, photo-Fenton reaction, and heterogeneous photocatalysis with TiO₂ are evaluated. The best results are obtained with the photo-Fenton process, for which more than 99% of the pharmaceutical is degraded within 5 minutes. At best experimental conditions the mineralization was superior to 75% after one hour of reaction.

Keywords – acetaminophen, photolysis, UV/H₂O₂, photo-Fenton, UV/TiO₂.

I. INTRODUCTION

The rapid development of industry and society runs parallel with the increasing generation of wastewaters, containing highly toxic and poorly biodegradable compounds. This situation affects the efficiency of conventional biological treatments, the most commonly used processes in wastewater remediation. The so-called “emerging pollutants” (pharmaceuticals and pesticides among others) generate an additional problem due to the scarce available information on their impact in the environment or their interferences with biological processes (Fent *et al.*, 2006). The presence of pharmaceutical compounds in water and wastewater has been repeatedly reported (Kümmerer, 2001; Ikehata *et al.*, 2006; Al Rifai *et al.*, 2007; Gagné *et al.*, 2006, Quesada Peñate *et al.*, 2009a). Many of these active substances are persistent as they are transparent to conventional wastewater

treatments and they are becoming ubiquitous in the environment (Carballa *et al.*, 2004; Tauxe-Wuersch *et al.*, 2005). Some of these compounds - in particular antibiotics, anti-tumor agents and analgesics - are indeed neither biodegradable, nor adsorbable on sewage sludge. Therefore, there has been an increasing concern about the impact of pharmaceutical compounds on public health and on the environment, not only because of their acute toxicity, but also their genotoxicity, as well as the development of pathogen resistance and endocrine disruption (Halling-Sørensen *et al.*, 1998; Graham *et al.*, 2011).

To drastically reduce the load of pharmaceutical compounds in discharged effluents, additional treatments have to be applied. Advanced oxidation processes (AOPs) have already proven to be effective for this purpose (Kolpin *et al.*, 2002, Ikehata *et al.*, 2006; Al Rifai *et al.*, 2007; McArdell *et al.*, 2011). AOPs can be performed either as a tertiary treatment after biological (secondary) treatment, or as a pre-treatment stage in order to enhance the biodegradability of trace organic contaminants.

AOPs are characterized by a variety of radical reactions that involve combinations of chemical agents (e.g. O₃, H₂O₂), heterogeneous catalysts (transition metals and metal oxides) and auxiliary energy sources (e.g. UV-vis radiation, electronic current, and ultrasound). UV based AOPs include UV/H₂O₂, UV/O₃, UV/H₂O₂/O₃, UV/H₂O₂/Fe²⁺ (or Fe³⁺), and UV/TiO₂. The efficiency of the various AOPs depends both on the rate of generation of free radicals and the extent of contact between the radicals and the organic compounds (Gogate and Pandit, 2004). In the Fenton reaction, hydroxyl radicals (HO•) are generated by the catalytic decomposition of H₂O₂ using Fe²⁺ in acidic medium (pH in the range 2–4) (Oliveros *et al.*, 1997). Photo-Fenton oxidation is the photo-catalytically enhanced version of the Fenton process. In this process, UV light irradiation increases HO• formation rate, and also improves the regeneration of the ferrous catalyst by reduction of Fe³⁺ and destruction of ferric complexes, thus allowing the

redox cycle to go on as long as H_2O_2 is available (Pignatello, 1992; Safarzadeh-Amiri *et al.*, 1996, 1997; Carneiro *et al.*, 2007). In UV/ TiO_2 process, titanium dioxide semiconductor absorbs UV light and generates radicals. Specifically, UV illumination of TiO_2 generates conduction band electrons and valence band holes. Band electrons interact with surface adsorbed molecular oxygen to yield superoxide radical anions, while band holes interact with water to produce hydroxyl radicals (Crittenden *et al.*, 2005; Chen *et al.*, 1997; Coronado and Soria, 2007).

Paracetamol (N-acetyl-4-aminophenol or acetaminophen, $\text{C}_8\text{H}_9\text{NO}_2$) is a common analgesic and antipyretic drug, heavily used all over the world. It has been detected in hospital effluents, but also in wastewater treatment plants, rivers and muds with concentrations in the range 6-65 $\mu\text{g}\cdot\text{L}^{-1}$ (Bound and Voulvoulis, 2006; Gómez *et al.*, 2006; Kinney *et al.*, 2006; Thomas *et al.*, 2007; Al Rifai *et al.*, 2007). Despite paracetamol is biodegradable (Sang *et al.*, 2007), its degradation rate is slow and does not allow its complete elimination by conventional wastewater treatment plants. On the other hand, chlorine treatment used for disinfection purpose is known to transform paracetamol into highly toxic intermediates, such as 1,4 benzoquinone and N-acetyl-p-benzoquinone imine (Bedner and Maccreehan, 2006). It is known that the hydrolysis of paracetamol is proton and hydroxyl ion catalyzed, while this breakdown process is minimal at a pH close to 6.

Several previous publications have been devoted to the study of paracetamol degradation in water using different advanced oxidation processes like radiolysis, sonolysis, catalytic wet air oxidation (CWAO) on activated carbon, ozonation and photolysis (Dalmázio *et al.*, 2008; Yang *et al.*, 2008; Andreozzi *et al.*, 2003; Quesada Peñate *et al.*, 2009b, 2012; Neamtu *et al.*, 2013; Aguinaco *et al.*, 2014; Torun *et al.*, 2014).

The oxidation of paracetamol promoted by UV/ TiO_2 in aqueous medium was investigated by Dalmázio *et al.* (2008), who obtained 90% of drug degradation and 35% of mineralization in two hours. Yang *et al.* (2008) studied photolysis and photocatalytic oxidation of acetaminophen to determine the optimal operating conditions for its degradation. UVA (365 nm) irradiation alone converted a negligible amount of paracetamol, whereas paracetamol concentration decreased substantially under UVC (254 nm) irradiation with marginal changes in total organic carbon (TOC). Paracetamol oxidation from aqueous solutions was also studied by means of ozonation and H_2O_2 photo-oxidation (Andreozzi *et al.*, 2003). Both oxidative systems were able to destroy the aromatic ring of the substrate with a partial conversion of the initial carbon content into carbon dioxide. For the adopted experimental conditions, mineralization yields up to 30% and 40% were observed with ozonation and H_2O_2 photo-oxidation, respectively. Main reaction intermediates and products were identified for both systems by HPLC-MS and GC-MS analyses (Andreozzi *et al.*, 2003). Neamtu *et al.* (2013) studied the degradation

of paracetamol in a bench-scale setup by means of simple ozonation (O_3) and ozonation enhanced by UV light (UV/ O_3). Both oxidative systems were capable of removing the substrate with mineralization yields up to 51% for ozonation and 53% for UV/ O_3 . The main advantage of photo-ozonation compared to simple ozonation was a more rapid conversion (92% vs. 79% after 90 min). The paracetamol decay followed a pseudo-first-order reaction with a superior rate constant (higher by 54%) for the UV promoted system in comparison with the direct ozonation. Mineralization was also slightly accelerated (+4%) in the UV/ O_3 system, due to the additional production of hydroxyl radicals induced by the UV light (Neamtu *et al.*, 2013). The oxidation of a mixture of paracetamol and sulfamethoxazole was carried out by means of single ozonation as initial process for in-situ production of hydrogen peroxide and in a subsequent step this hydrogen peroxide was used for a sequential treatment in combination with Fenton or photo-Fenton systems (Aguinaco *et al.*, 2014). From single ozonation, fast and complete elimination of both pharmaceuticals was achieved, but at the end of the ozonation step only 10% of total organic carbon was removed. The addition of ferrous ions to the reaction media after single ozonation did not improve the extent of mineralization. Conversely, the application of photo-Fenton process resulted in a markedly increase in the mineralization efficiency, nevertheless total mineralization was not attained. A simple kinetic model of the processes allowed the calculation of pseudo-first order kinetic constants. Higher rate constants for the photo-Fenton system were due to the photochemical regeneration of ferrous ions (Aguinaco *et al.*, 2014).

In this work, the effect of several operating conditions on paracetamol removal efficiency, namely pH and initial concentrations of H_2O_2 , Fenton reagent and TiO_2 , was studied. In addition, the mineralization of the substrate was also evaluated.

II. MATERIALS AND METHODS

A. Materials

$\text{C}_8\text{H}_9\text{NO}_2$ (99 %), $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ as the source of Fe^{2+} , H_2SO_4 (95-97 %) and NaOH (99 %) were all provided by Sigma-Aldrich. TiO_2 PC 500 catalyst was supplied by Millennium. It was characterized by its anatase structure (> 99 %), with crystallite diameter between 5 and 10 nm. H_2O_2 (30 % w/w) and H_3PO_4 (85 %) were purchased from Fluka. HPLC eluent acetonitrile ($\text{C}_2\text{H}_3\text{N}$) was provided by Scharlau-Chemie. Ultrapure water supplied by Purelab Option system (Elga) was used throughout the study. For all experiments, the initial concentration of paracetamol was 100 $\text{mg}\cdot\text{L}^{-1}$.

B. Photolysis, H_2O_2 photo-oxidation and photo-Fenton experiments

The corresponding experimental set-up is displayed in Fig. 1. It is composed of a 1L Pyrex reactor coupled to a 0.5 L glass photochemical reactor. The latter includes a medium-pressure mercury vapor lamp (450W Hanovia PC451.050 lamp, arc length 4.8 cm) placed in a jacketed borosilicate glass immersion well. Of total energy radi-

ated, approximately 40-48 % is in the ultraviolet portion of the spectrum (with a maximum at 366 nm), 40-43 % in the visible, and the balance in the infrared. The glass lamp holder completely cuts off wavelengths shorter than 280 nm, about 50% of the emission at 310 nm and results in 94% transmittance above 355 nm.

Both reactors are connected to a thermostat for temperature control ($30 \pm 1^\circ\text{C}$). The solution circulates between the reactors by means of a peristaltic pump at a flow rate of $80 \text{ mL}\cdot\text{min}^{-1}$ and it is continuously stirred in both reactors.

The direct photolysis was carried out at three pH values (2.6, 5.5 and 8.0) adjusted with H_2SO_4 or NaOH . In the $\text{UV}/\text{H}_2\text{O}_2$ experiments, oxidant concentration was varied between 13.9 and $41.7 \text{ mmol}\cdot\text{L}^{-1}$, corresponding to 1 to 3 times the stoichiometric amount for complete mineralization.

For the photo-Fenton oxidation, different combinations of Fe^{2+} ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) and H_2O_2 concentrations were applied following a 2^2 factorial design plan (Fe^{2+} : 0.30 and $0.90 \text{ mmol}\cdot\text{L}^{-1}$; H_2O_2 : 13.9 and $41.7 \text{ mmol}\cdot\text{L}^{-1}$).

C. TiO_2 photocatalysis experiments

Photocatalysis experiments were carried out in a 1 L cylindrical Pyrex reactor with air injection to provide oxygen and magnetic stirring. Reaction temperature was set to $30 \pm 1^\circ\text{C}$. A low-pressure mercury lamp (Philips PL-L 24W/10/4P model with a maximum emission at 365 nm and a measured light intensity of $47.5 \text{ W}\cdot\text{m}^{-2}$) was used and placed in a thermo-regulated cylinder. TiO_2 concentration was varied from 0 to $3 \text{ g}\cdot\text{L}^{-1}$. This experimental set-up is shown in Fig. 2.

D. Chemical analysis

Oxidation experiments were carried out during 5 hours, during which samples were taken at regular time intervals to follow the evolution of paracetamol conversion and mineralization. Photo-Fenton samples were preliminary treated with a quenching solution (NaOH $0.1 \text{ mol}\cdot\text{L}^{-1}$) that precipitated iron. This precipitate was removed by $0.2 \mu\text{m}$ nylon filters. Photocatalysis samples were passed through the same filters to eliminate powdered TiO_2 .

For all the processes, liquid samples were characterized using a liquid chromatograph equipped with a UV/Vis detector (Varian ProStar 310). Paracetamol was separated from oxidation intermediates on a Prontosil C18 reversed phase column, using a 90:10 mixture of acidified water (pH 2.2) and acetonitrile as isocratic mobile phase (flow rate of $0.25 \text{ mL}\cdot\text{min}^{-1}$). The detection of the compound was achieved at a wavelength of 254 nm.

To monitor the mineralization level, the residual TOC was measured on a SHIMADZU TOC-V CSN analyzer equipped with a non-dispersive infrared detector. The TOC values were obtained from the difference between the Total Carbon (TC) and Inorganic Carbon (IC) contents of the samples. For TC, the combustion reaction was achieved at 680°C on a platinum catalyst, using oxygen flow at $150 \text{ mL}\cdot\text{min}^{-1}$. IC was measured by addition of HCl 2N and CO_2 degassing through

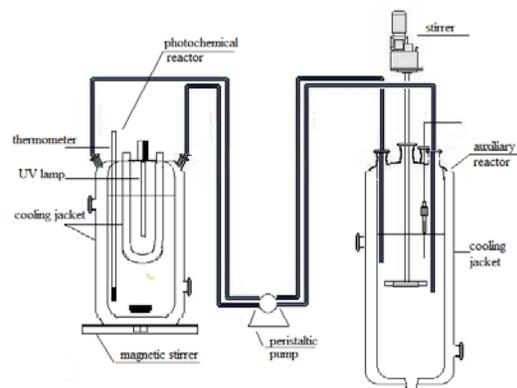


Fig. 1. Experimental set-up for photolysis, $\text{UV}/\text{H}_2\text{O}_2$ and photo-Fenton oxidation.

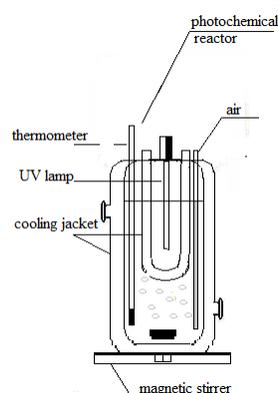


Fig. 2. Experimental set-up for heterogeneous photocatalytic degradation.

Table 1. Conversion of paracetamol (%) by non-catalytic photo-processes

Process	pH ₀	H_2O_2 , $\text{mmol}\cdot\text{L}^{-1}$	Time, min			
			10	60	180	300
UV	2.6	-	0.7	0.9	2.5	4.2
	5.5	-	0.5	1.3	1.2	1.2
	8.0	-	0.7	0.9	1.0	3.0
$\text{UV}/\text{H}_2\text{O}_2$	2.6	13.9	1.1	7.8	19.9	26.7
	2.6	41.7	2.8	8.2	27.1	29.2
	5.5	13.9	0.7	5.2	28.4	41.3
	5.5	27.8	3.6	30.0	57.7	69.0
	5.5	41.7	2.5	21.6	58.6	68.8

nitrogen sparging.

III. RESULTS AND DISCUSSION

Table 1 shows the results of paracetamol photo-degradation for non-catalytic processes. The initial pH value (pH₀) was varied to study its effect on the considered processes. During the oxidation, the pH of the reaction medium usually decreased due to the formation of acidic intermediates (final pH ranging between 3.0 and 5.0).

Irrespective of the pH value, the degradation rate of paracetamol by photolysis at $\lambda > 280 \text{ nm}$ was almost negligible, a maximum conversion of 4.2% being achieved after 5 hours with $\text{pH}_0 = 2.6$. It is known that

the hydrolysis of paracetamol is proton and hydroxyl ion catalyzed, while this breakdown process is minimal at a pH close to 6 (Koshy and Lach, 1961). Previous works confirmed that at pH between 3.7 and 5.5 UVA-vis radiation only results in a poor removal of the molecule, as a consequence of its weak absorption within the range 300 to 800 nm (Yanxiang *et al.*, 2010; Aguilar *et al.*, 2011).

The addition of H₂O₂ improved the pollutant conversion, and the best results were obtained for medium pH₀ (5.5) and oxidant dose (27.8 mmol.L⁻¹). Under these conditions, 30% of paracetamol was eliminated after 60 minutes of reaction. Still, the TOC conversion reached less than 10% after 5 hours of reaction for all the conditions. Indeed, H₂O₂ does not absorb significantly beyond 300 nm and the production of HO• should remain low under the applied light irradiation.

Photocatalysis with TiO₂ irradiated at 365 nm yielded a paracetamol conversion of more than 60% at near-neutral pH (Fig. 3), but no effect of the catalyst concentration was found in the investigated range (0.3-3 g.L⁻¹). Such a plateau was already observed and attributed to the opposite effects between the increase in active surface and decrease of light penetration when increasing TiO₂ concentration (Aguilar *et al.*, 2011). While greater catalyst concentrations increase available active sites, light penetration in the reaction system decreases, activating a reduced amount of TiO₂ in the suspension. On the other hand, at a higher catalyst loading, the originally activated TiO₂ may be deactivated through collision with ground-state catalyst according to the equation:



where TiO₂* has active species adsorbed on its surface and TiO₂# is the deactivated form of TiO₂ (Yang *et al.*, 2008). Large catalyst concentrations would also cause agglomeration and sedimentation of TiO₂, reducing the available catalyst surface for photon absorption. All these reasons might explain the negligible increase in paracetamol degradation beyond an optimal TiO₂ dosage, 0.5 g.L⁻¹ in this study. The present results are also in line with the work of Yang *et al.* (2008), which observed that more than 95% of 2.0 mM paracetamol was degraded within 80 min under UVC in the presence of TiO₂ 0.4 g.L⁻¹, with no improvement over 0.8 g.L⁻¹ of catalyst. In our conditions, the TOC conversion after 4 hours was about 30% with 0.3 g.L⁻¹ of TiO₂.

On the other hand, photo-Fenton oxidation achieved over 99% conversion of paracetamol within only five minutes. Table 2 shows the levels of pollutant mineralization for this process. For the highest quantity of catalyst and oxidant the mineralization yield was superior to 75% after one hour of reaction, outperforming the results of the other photo-processes under UVA(B)-vis light irradiation. In other words, photo-Fenton oxidation was found the best process for paracetamol destruction and the contribution of concomitant non-catalytic photo-processes (direct photolysis and UV/H₂O₂) remained very low.

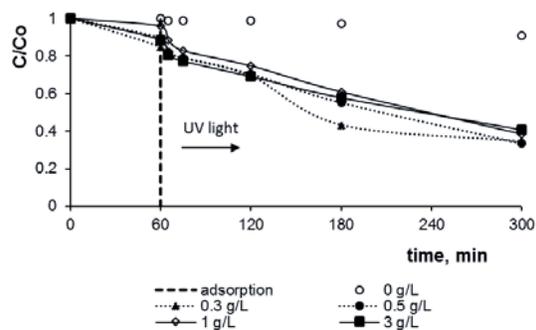


Fig. 3. Photocatalytic degradation of paracetamol at different TiO₂ concentrations.

Table 2. Mineralization of paracetamol (%) by photo-Fenton process (pH=2.6; n.a.: non available)

H ₂ O ₂ , mmol.L ⁻¹	FeSO ₄ x 7H ₂ O, g	Time, min				
		5	10	60	180	300
13.9	0.13	7.0	21.0	64.3	74.7	80.7
13.9	0.38	6.3	29.3	73.0	82.1	84.5
41.7	0.13	12.3	28.0	65.7	83.4	84.2
41.7	0.38	21.1	n.a.	76.2	84.7	92.2

A similar performance was reported by Santos-Juanes Jordá *et al.* (2011) at a pilot plant scale: a solution of 157.5 mg.L⁻¹ paracetamol was satisfactorily decontaminated by 15 minutes of photo-Fenton treatment with 20 mg.L⁻¹ of Fe²⁺ and 200 mg.L⁻¹ of H₂O₂, yielding more than 20% TOC conversion. Indeed, from bioassays performed with *P. putida* the authors concluded that the biodegradability efficiency increased from 30% for untreated paracetamol solution to about 70% for a mineralization yield of ca. 20% (complete biodegradability being achieved over 72% of mineralization).

Finally, the efficiency of UV-induced AOPs can be compared to that of other oxidation processes carried out in our previous works: catalytic wet air oxidation (CWAO) over activated carbon (Quesada Peñate *et al.*, 2012) and high frequency ultrasound (Quesada Peñate *et al.*, 2009b). None of these techniques could compete with the results of photo-Fenton oxidation (at optimal conditions), as they did not exceed 60% mineralization yield after 2 hours.

IV. CONCLUSIONS

Efficient degradation of paracetamol in aqueous solution could be achieved by a combination of UV-vis irradiation ($\lambda > 280$ nm) with Fenton reagent, yielding mineralization level as high as 75% in one hour. Conversely, direct photolysis, UV/H₂O₂ and photocatalysis with TiO₂ resulted in only a partial conversion of the pollutant after 4-5 hours, with a mineralization yield lower or only slightly higher than the required value of 20% reported by Santos-Juanes Jordá *et al.* (2011) for an efficient detoxification.

To confirm this conclusion, next study will focus on the investigation of the biodegradability improvement with the perspective of an integrated process together with biological treatment.

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