Use of the photo-Fenton process to discover the degradation of drugs present in water from the Wastewater Treatment Plants of the pharmaceutical industry

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Uso del proceso foto-Fenton para descubrir la degradación de los fármacos presentes en agua en las Plantas de Tratamiento de Aguas Residuales de la industria farmacéutica

Us del procés foto-Fenton per descobrir la degradació dels fàrmacs presents en l'aigua en les Plantes de Tractament d'Aigües Residuals de la industria farmacèutica

SUMMARY

Advanced oxidation processes (AOP) have been used in effluent treatment in order to degrade the composites that persist in the environment even after conventional treatment. This work employs AOP (known as the photo-Fenton process) to study the degradation of the pharmaceutical acetylsalicylic acid, diclofenac, dipyrone and paracetamol in different effluents from Wastewater Treatment Plants (WWTPs). The data collected from the different effluents, which were obtained by mean of a chromatographic analysis, showed that 3 out of the 4 pharmaceuticals analysed were detected in concentrations that ranged from $0.29 \, mg \cdot L^{-1}$ to $3.96 \, mg \cdot L^{-1}$. The photodegradation study using UV-C radiation showed that the photo-Fenton process managed to degrade between 71.9% and 100% of the pollutants. Furthermore, it promoted the conversion of 66.5% of organic material, as the lumped kinetic model satisfactorily represents the kinetics of the process. The toxicity trials verified that the photo-Fenton process did not generate toxic intermediaries once the seeds had germinated.

Keywords: Pharmaceuticals; effluents; photo-fenton; kinetic modelling.

RESUMEN

Se han utilizado procesos de oxidación avanzados (AOP) en el tratamiento de efluentes con el fin de degradar los compuestos que persisten en el entorno incluso después de un tratamiento convencional. Este trabajo utiliza AOP (conocido como el proceso foto-Fenton) para estudiar la degradación del ácido acetilsalicílico farmacéutico, el diclofenac, la dipirona y el paracetamol en distintos efluentes de las Plantas de Tratamiento de Aguas Residuales. Los datos recogidos de los diferentes efluentes, que han sido obtenidos por medio de un análisis cromatográfico, demostraban que 3 de los 4 productos farmacéuticos analizados se detectaban en concentraciones que oscilaban entre $0.29 \, mg \cdot L^{-1}$ y $3.96 \, mg \cdot L^{-1}$. El estudio de fotodegradación que utiliza la radiación UV-C demostraba que el proceso foto-Fenton conseguía degradar entre un 71.9% y un 100% de los agentes contaminantes. Además, promovía la conversión del 66.5% del material orgánico, ya que el modelo cinético agrupado representa satisfactoriamente la cinética del proceso. Los ensayos de toxicidad verificaban que el proceso foto-

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Fenton no generaba sustancias intermedias tóxicas una vez se habían germinado las semillas.

Palabras clave: Productos farmacéuticos; efluentes; foto-fenton; modelo cinético.

RESUM

S'han utilitzat processos d'oxidació avançats (AOP) en el tractament de efluents amb la finalitat de degradar els compostos que persisteixen en el entorn inclús desprès d'un tractament convencional. Aquesta feina utilitza AOP (conegut com el procés foto-Fenton) per estudiar la degradació del àcid acetilsalicílic farmacèutic, el diclofenac, la dipirona y el paracetamol en diferents efluents de les Plantes de Tractament d'Aigües Residuals. La informació recollida dels diferents efluents, que ha sigut obtinguda per mitja d'un anàlisi cromatogràfic, demostrava que 3 de 4 productes farmacèutics analitzats es detectaven en concentracions entre 0.29mg·L⁻¹ i 3.96mg·L⁻¹. El estudi de fotodegradació que utilitza la radiació UV-C demostrava que el procés foto-Fenton aconseguia degradar entre un 71.9% i un 100% dels agents contaminants. A més que promovia la conversió del 66.5% del material orgànic, perquè el modelo cinètic agrupat representa satisfactòriament la cinètica del procés. Els tests de toxicitat verificaven que el procés foto-Fenton no generava substancies intermèdies tòxiques una vegada germinades les llavors.

Paraules clau: Productes farmacèutics; efluents; foto-fenton; model cinètic.

1. INTRODUCTION

This type of substance has been encountered owing to the increased production and consumption of pharmaceuticals, which are present in different aqueous matrices and are derived from domestic sewage, and principally from Wastewater Treatment Plants. Pharmaceuticals have a shelf-life that frequently encourages their disposal, which eventually damages the environment[1-2].

Several pharmaceuticals are found in surface waters, industrial and domestic effluents, within which are acetylsalicylic acid (ASA), diclofenac and ibuprofen. These types of pharmaceuticals have been identified in countries such as Germany[3], Brazil[4-5], Spain[6] and Sweden[7]. In developing countries, such as Brazil, nonsteroidal anti-inflammatories (NSAIDS), analgesics and antipyretics are usually self-prescribed since a medical prescription for these types of pharmaceuticals is not required. This enhances the presence of these pollutants in rivers and domestic wastewater treatment plants.

The need for alternative treatments, known as polishing treatments, is increasing, since the presence of different classes of pollutants is also gradually increasing. Studies show that advanced oxidative processes (AOP), such as ozonization, Fenton, photo-Fenton and photocatalysis, are regarded as technologies that are capable of promoting the degradation of micropollutants and the conversion of organic matter[8-9]. However, very little research has been carried out into the photo-Fenton AOP, which consists of a mixture of ferrous salts and ultra-violet radiation (UV)[10-11], thus avoiding or reducing the addition of this composite and making it more economically viable. Some authors have described its efficiency as regards dye decolourisation and the degradation of polycyclic aromatic hydrocarbons (PAH)[12-15]. Nevertheless, there have been limited reports concerning the use of this process in the degradation of the pharmaceuticals diclofenac, dipyrone, paracetamol, and acetylsalicylic acid when using the photo-Fenton process.

The aim of this work is, therefore, to study the photodegradation of the following pharmaceuticals: acetylsalicylic acid (ASA), diclofenac, dipyrone and paracetamol, all of which are present at the exit points of certain WWTPs, using the photo-Fenton advanced oxidative process. The efficiency of the treatment was verified by quantifying the concentration levels of the pharmaceuticals and the organic matter mineralisation levels, thus making it possible to create a kinetic model of the sample being studied. The risks caused by the formation of intermediate compounds after the use of the AOP was evaluated by studying the acute toxicity through the use of germination analysis and root growth on different types of seeds.

2. MATERIALS AND METHODS

2.1 Data collection and sample characterisation

The data was collected before and after the treatment of effluence at three WWTPs (one appertaining to the Pharmaceutical Industry and the other two to domestic sewage). In order to evaluate the efficiency of the conventional treatment processes at these WWTPs, physicochemical analyses of effluents were run. The quality parameters analysed were: (i) chemical oxygen demand (COD), (ii) biochemical oxygen demand (BOD), (iii) total solids (TS), (iv) total volatile solids (TVS), (v) total fixed solids (TFS), (vi) pH and (vii) iron (Fe), using the Standard Methods for the Examination of Water and Wastewater. The presence of the following pharmaceuticals in exit water at each of the WWTPs was subsequently evaluated: (i) acetylsalicylic acid, (ii) diclofenac, (iii) dipyrone and (iv) paracetamol.

2.2 Analytical methods for pharmaceutical detection

The composites were quantified and identified using Shimadzu HPLC equipment, with an ULTRA C18 column with reverse phase analysis (5μm; 4.6 x 250 mm) and UV detection (SPD-20A) for wavelengths of 285nm. The mobile phase employed consisted of an acidified water solution with 10% of acetic acid and acetonitrile at a volumetric ratio of 65:35. The oven

temperature of the equipment was maintained at 40 ±1°C with a 0.700 mL·min^{-1} flow and a pressure of 53kgf·cm^{-2}.

The active pharmaceutical ingredients (API) were supplied by the pharmaceutical industry from which the effluent was collected, and had the following purity levels: ASA (100.24%), declofenac (99.07%), dipyrone (100.02%) and paracetamol (99.67%). The composites were detected on the basis of their retention time, and the method used had previously been validated according to the requirements of the Brazilian regulatory agencies, ANVISA and INMETRO. The studied composites were detected (wavelength of 285nm) with a retention time of: ASA (4.0 – 4.2mins), diclofenac (8.7 – 9.3mins), dipyrone (2.8 – 3.0mins) and paracetamol (3.5-3.8mins).

In order to determine the pharmaceuticals in wastewater, the samples were prepared by employing a solid-liquid extraction process using strata-X polymeric cartridges operating in reverse phase (500mg/6mL – Allcrom). This procedure was carried out using a Wilson peristaltic pump (USA) operating under a 10 mL·min^{-1} flow rate; the stationary phase was conditioned with two aliquots of 3mL of acetonitrile (Merck), after which two aliquots of 3mL of ultrapure water were added. Once the cartridges had been conditioned, the effluent under study was then filtered (Figure 1) and collected in a 5mL volumetric flask, and its volume measured with acetonitrile.
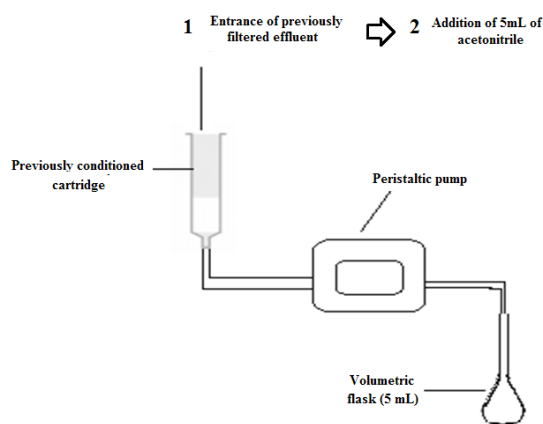

Figure 1- Schematic diagram of the extraction and concentration phase of the sample studied.

2.3 Use of the photo-Fenton process

The photo-Fenton AOP was studied using a bench reactor of low operational cost, which consisted of a wooden box of the following dimensions: 50cm x 32cm x 37cm. In order to promote radiation, three UV-C radiation lamps (of 30 W each) operated in parallel. For this study, 2L of the effluent were submitted to the photo-Fenton process.

In order to perform the trials, 2mL of H$_2$O$_2$ were added every 30mins for a total period of 120mins. A total volume of 10mL of hydrogen peroxide was added. The iron used to perform the AOP was in its endogenous form, and its concentration was determined through the use of an atomic absorption analysis.

2.4 Kinetic modelling

The kinetic modelling of the process of pharmaceutical degradation in the effluents was verified and studied using the Lumped Kinetic Model – LKM [16], which is also known as the grouped kinetic model. This type of modelling takes into account the total organic carbon (TOC) index, which describes the total residual concentration profile in terms of the carbon contained in the liquid phase under very limited conditions. The TOC analyses were performed with Shimadzu high-sensitivity equipment (TOC-Vcsh model, OCT-1 sampler) capable of carrying out analyses in the range of 4 ng·L^{-1} to 2500 mg·L^{-1}. The TOC values were quantified by means of the difference between total carbon (TC) and total inorganic carbon (TIC) concentrations.

Researchers have employed this method to describe the total residual concentration profile (C_t), in terms of carbon, contained in the liquid phase[17]. The trials with which to determine the kinetics of the process (TOC index over time) were run under the following conditions: the addition of 2mL of H$_2$O$_2$ at 0, 30, 60, 90 and 120 min, with a total volume of 10mL of this reagent.

2.5 Toxicity studies

An analysis was performed in order to evaluate the toxic level of reaction intermediates formed after the photo-Fenton process. This consisted of exposing *Impatiens balsamina* (balsamine) and *Celosia cristata* (cockscomb) seeds to different concentrations of the liquid waste, without alteration, for 120 hours. Toxicity tests were similarly run using *Americano Hard* (wheat) grains for a period of 72 hours[18].

A Petri dish and filter paper were used as support in the bio-trials. The trials were run in concentrations of: 100%, 70%, 50%, 5% and 1% of the effluent. 10 seeds/grains and 2mL of test-solution were added to the filter paper in each dish. Water was used for the negative control, while Boron, in the form of a boric acid solution, was used as positive control in the sensitivity test. The Petri dishes were maintained at a temperature of 25±1°C without any exposure to light.

The seeds that germinated coherently with the negative control were subsequently observed. The root growth of each species was verified, thus making it possible to calculate the relative growth rate (RGR) and the germination rate (GR), according to Equations 1 and 2, respectively[19].

$$RGR = \frac{(RLS)}{(RLC)} \quad (1)$$

$$GR = RGR\frac{(SGS)}{(SGC)} \times 100 \quad (2)$$

In which RLS is the total root length of the sample; RLC is the total root length in the negative control; SGS is the number of seeds germinated in the sample, and SGC is the number of seeds germinated in the negative control.

3. RESULTS AND DISCUSSION

3.1 Characterisation of the samples

The physicochemical analyses were carried out according to the Standard Methods for the Examination of Water and Wastewater and the data obtained were analysed in conformance with the CONAMA 430 effluent requirements[20], as presented in Table 1.

Table 1: *Average results of the quality parameters of the WWTPs.*

Analysis	WWTP1*		WWTP2*		WWTP3*		CONAMA 430/2011
	Entrance	Exit	Entrance	Exit	Entrance	Exit	
COD (mg·L^{-1} of O$_2$)	1458.03	396.10	1006.42	339.98	194.96	95.6	-
BOD (mg·L^{-1} of O$_2$)	586.07	174.50	600	70	117.5	37.5	<120 or 60% removal
TS (mg·L^{-1})	407.67	227.80	888	659	462.5	563	<500
TVS (mg·L^{-1})	245.00	71.17	384	237	322	417	-
TFS (mg·L^{-1})	162.67	119.00	504	422	140.5	146	-
pH	9.79	5.86	7.6	7.44	6.48	6.6	5≤ pH ≤9
Fe (mg·L^{-1})	0.67	0.63	ND	ND	ND	ND	< 15.0

*WWTP 1 = Pharmaceutical Industry; WWTP 2 = Domestic Sewage; WWTP 3 = Domestic Sewage
ND = Not detected

The pH values were accordance with the standards of discharge of effluents (a pH of between 5 and 9) for the three plants analysed, while the COD and the BOD remained within the range of values accepted. The TS values at the exit of WWTPs 2 and 3 were not within the regulated values, and had values of 659mg·L^{-1} and 563mg·L^{-1}, respectively[20]. This increase was owing to the residual solids released by a fire in the woods surrounding the WWTP, which contributed to it not meeting the legislation requirements for such parameters.

3.2 Detection of pharmaceuticals in the effluents surrounding the WWTPs.

A previously validated method made it possible to identify and quantify the 4 pharmaceuticals under study in an exact manner. The chromatographic determination (HPLC) was carried out by taking into consideration the retention time of each of the samples studied, along with the wavelength analysed (285nm). The samples were analysed after being submitted to the pre-treatment procedure, using the solid-phase extraction. Table 2 shows the results of the concentrations of the pharmaceuticals in the different samples analysed. The drug degradation was analysed by carrying out a kinetic study, while the toxicity was evaluated using the effluent with the highest concentrations of the pharmaceuticals being studied.

The emission of photons of UV-C radiation was initially measured using a radiometer (Emporionet), which was equal to 1.44 mW·cm^{-2}. The results depicted in Table 2 show that three out of the four pharmaceuticals studied were present in the aquatic ecosystem in what are considered to be high concentrations (µg·L^{-1} a pg·L^{-1}), bearing in mind that these levels are classified as emerging contaminants[21]. Once the presence of these pharmaceuticals had been detected, the degradation study proceeded through the use of the AOP.

Table 2: *Identification and quantification of the ASA, diclofenac, dipyrone and paracetamol in the different samples analysed.*

Pharmaceutical	WWTP1 Exit	WWTP2 Exit	WWTP 3 Exit
Acetylsalicylic Acid	0.65 mg·L^{-1}	ND[**]	0.29 mg·L^{-1}
Diclofenac	ND[**]	ND[**]	ND[**]
Dipyrone	3.92 mg·L^{-1}	1.05 mg·L^{-1}	0.65 mg·L^{-1}
Paracetamol	1.57 mg·L^{-1}	0.79 mg·L^{-1}	0.80 mg·L^{-1}

[*] DL_{ASA} (Detection limit of the ASA) = 0.19 mg·L^{-1}; [**] Not Detected

3.3 Analysing Pharmaceutical Degradation with the photo-Fenton process

A previous study on the efficiency evaluation of the photolysis process in a UV-C radiation reactor showed low percentages of AAS (37.20% ± 2.69) and diclofenac (32.40% ± 1.63) degradation. The study also obtained a degradation of (78.50% ± 0.28) of paracetamol. However, the UV/H$_2$O$_2$ system was more efficient and degraded 100% of the 3 drugs[22]. The photo-Fenton was, therefore, the process chosen, since the effluent present in its constitution iron and the presence of H$_2$O$_2$ is primordial as regards promoting the degradation of ASA and diclofenac.

In order to analyse the pharmaceutical degradation, samples derived from the exit of the WWTP1 were used. Furthermore, these samples had the highest contamination level of the pharmaceuticals studied from the three WWTPs analysed.

This effluent was doped with diclofenac, bearing in mind that this pharmaceutical was not initially present in the sample. An aliquot from the effluent was subsequently collected in order to quantify the concentration of diclofenac, now present in the effluent, which was of 4.04 mg·L^{-1}.

An analysis to determine the concentration of iron in the sample of the effluent from WWTP1 was then run, after employing an atomic absorption analysis to verify that this metal was present at a concentration of 0.63 mg·L^{-1}. The efficiency of the AOP employed was evaluated through the use of a chromatographic analysis, following the same procedure described for the effluent without the polishing treatment. The quantification of the four pharmaceuticals studied and the degradation evaluation of each composite are displayed in Table 3.

It is important to highlight that the diclofenac was added to the effluent from the pharmaceutical industry Wastewater Treatment Plant, since it was produced by the company from which the effluent was collected. However, the industry was not producing it at the time of collection. It is also known that this compound is located in different aquatic bodies[23,24] which led us to study its degradation.

Table 3: *Degradation analysis of the pharmaceuticals after the AOP for a period of 150mins and the total addition of 10mL of H_2O_2.*

Pharmaceutical	Initial concentration (mg.L⁻¹)	Final concentration (mg.L⁻¹)	Pharmaceutical degradation (%)
Acetylsalicylic Acid	0.65	0.18 < DL	≈ 71.90%
Diclofenac	4.04	ND	100.00%
Dipyrone	3.92	0.09 <DL	≈ 97.60%
Paracetamol	1.57	ND	100.00%

< DL = less than the Detection Limit; ND = Not detected

The data presented in Table 3 demonstrate the efficiency of the photo-Fenton process, and the pharmaceutical degradation levels were observed to be between 71.90 and 100.00%. Studies have reported degradation levels for pharmaceutical compounds that varied between 62.60% and 95.70%[25].

Having noted that the AOP employed was effective in the degradation of the pharmaceuticals under study, the conversion/mineralisation analysis of the organic matter then took place. Table 4 presents the results of the TOC conversion indexes.

Table 4: *TOC conversion monitoring over time, with the addition of 2mL of H_2O_2 every 30 mins.*

Exposure time (mins)	Volume of H_2O_2 accumulated (mL)	TOC (mgC·L⁻¹)	TOC Conversion (%)
0	2	167.10	0.00%
30	4	152.05	9.01%
60	6	134.40	19.57%
90	8	101.20	39.44%
120	10	78.22	53.19%
150	---	55.99	66.49%

The results presented in Table 4 enabled us to verify the mineralisation of the compounds, which was attested through the use of a TOC analysis. The pollutants present in the effluent after a period of 120mins attained conversion rates of above 53%, in accordance with the mineralisation studies, which obtained conversions of around 40% for this period of time[3,26]. It is known that the degradation of pharmaceutical compounds leads to the formation of intermediary organic compounds, which indicates the impossibility of the total TOC conversion indexes. This makes it possible to once again consider an optimum mineralisation of the organic matter when increasing the time of the experiment.

3.4 Kinetic Modelling

Having obtained the experimental results of the TOC in the effluent after applying the photo-Fenton process on a bench reactor, the kinetic modelling was then built in order to calculate the relation between the TOC and TOC_0 (Initial TOC). The results of this are presented in Table 5.

The lumped kinetic modelling expresses the concentrations of the composites in different groups: species "A" comprises the initial contaminant (pharmaceuticals) and intermediates susceptible to oxidation (non-refractory). "B" represents all refractory organic spe-

Table 5: *Conversion of the organic matter in time and determination of the ratio: TOC over time: Initial TOC (observed and calculated).*

t (mins)	TOC	TOC/TOC_0 (Observed)	TOC/TOC_0 (Calculated)
0	167.2	1.00	1.00
15	160.09	0.96	0.97
30	152.05	0.91	0.92
60	134.4	0.80	0.77
90	101.2	0.61	0.61
120	78.22	0.47	0.48
150	55.99	0.33	0.37
180	53.87	0.32	0.28

cies owing to the oxidation of "A". "C" involves all the carbon dioxide formed from the complete oxidation of the organic species (complete mineralisation, CO_2 + H_2O). Let us consider the following groups:

- C_A: Concentration of residual carbon of the most non-refractory intermediary pharmaceuticals;
- C_B: Concentration of intermediary refractory carbon.

C_A and C_B can be expressed according to Equations 3 and 4, and represent the concentrations of residual carbon relative to the concentration of initial total organic carbon (TOC_0):

$$C_A = \frac{\text{Most}-\text{intermediary non}-\text{refractory carbon of the selected pharmaceuticals}}{[TOC_0]} \quad (3)$$

$$C_B = \frac{\text{Intermediary refractory carbon}}{[TOC_0]} \quad (4)$$

When considering the bench reactor (with UV-C radiation) operating in a batch mode with a constant liquid volume and temperature, and with the mass accumulation flow rate of each component thus being equal to the reactive flow, it was then possible to determine differential Equations 5 and 6.

$$-\frac{dC_A}{dt} = (k_1 + k_2)C_A \quad (5)$$

and

$$\frac{dC_B}{dt} = k_2 C_A - k_3 C_B \quad (6)$$

By integrating Equations 4 and 5 and considering $C_r = C_A + C_B$ in t = 0, C_{A0} = 1 and C_{B0} = 0 it is possible to describe the TOC concentration profile present in the liquid phase over the reaction time, according to the proposed model (Equation 7).

$$\frac{TOC}{TOC_0} = C_r = \frac{k_1-k_3}{k_1+k_2-k_3}e^{-(k_1+k_2)t} + \frac{k_2}{k_1+k_2-k_3}e^{-k_3t} \quad (7)$$

The values obtained for the constants k_1, k_2 and k_3 were: 0.0264min⁻¹, 0.0092min⁻¹ and 0.0002min⁻¹, respectively. The study of the constants allowed us to verify that the mineralisation of the most intermediary non-refractory pharmaceuticals (k_1 = 0.026 min⁻¹) occurs at a higher reaction rate than its degradation in non-refractory intermediaries (k_2 = 0.0092 min⁻¹), while the mineralisation of the non-refractory intermediaries had a very low reaction rate (k_3 =

0.0002min⁻¹) when compared to the remaining reactions involved. These analyses make it possible to perform a simplification of the model, considering $k_3 \to 0$, with Equation 6 rewritten as shown in Equation 8[27].

$$\frac{TOC}{TOC_0} = C_r = \frac{k_1}{k_2}e^{-(k_1+k_2)t} + \frac{k_2}{k_1+k_2} \quad (8)$$

The graph concerning the conversion of organic matter over time (Figure 2(a)) confirms that the kinetic model proposed satisfactorily represents the temporal evolution of the TOC conversion, with a correlation coefficient of 0.992. Figure 2(b) shows a comparison of the results of the calculated and experimental residual fractions (TOC/TOC$_0$). This ratifies that the grouped kinetic model adequately describes the experimental results; the better adjustment of the model, the closer the points are to the first bisector.

In order to verify the residual data distribution in a symmetric form around the axis, a graph was plotted (Figure 2(c)), which determines the reliability of the experimental points.

The reliability of the model can be verified when the distribution of the experimental and theoretical values is analysed. These values are distributed along the trend line of the theoretical values and do not obtain deviations higher than 0.04, as demonstrated in Figure 2 (c).

3.5 Toxicity analysis

After applying the photo-Fenton process, the toxicity of the substances formed on the *Impatiens balsamina* (balsamine), *Celosia cristata* (cockscomb) and *Americano Hard* (wheat) seeds during the process was analysed. We first ran the germination tests on the seeds and the grains under analysis, in addition to the positive and negative controls (no seed or grain germinated when using boric acid). The results obtained for the average seeds germinated in each trial are shown in Table 6.

An analysis of Table 6 shows that, for the wheat grain (*Americano Hard)* and balsamine flower (*Impatiens balsamina*), the effluent reacted in the same way as in the negative control for the different concentrations analysed. It is thus possible to state that a similar germination behaviour was observed on the grain and flower after the AOP treatment and for those in presence of water, indicating that the compounds formed were not toxic. With regard to the cockscomb seed (*Celosia cristata*), the reaction of the effluent at 1.5% and 10% was similar to the reaction for the negative control, having verified the reduction in the germination when the amounts of effluent analysed were of: 50, 70 and 100%, respectively. Once the germination had been observed, the root growth was then analysed, and the average values obtained for each of the trials run are presented in Table 7.

Table 6: *Average number of seeds/grains germinated.*

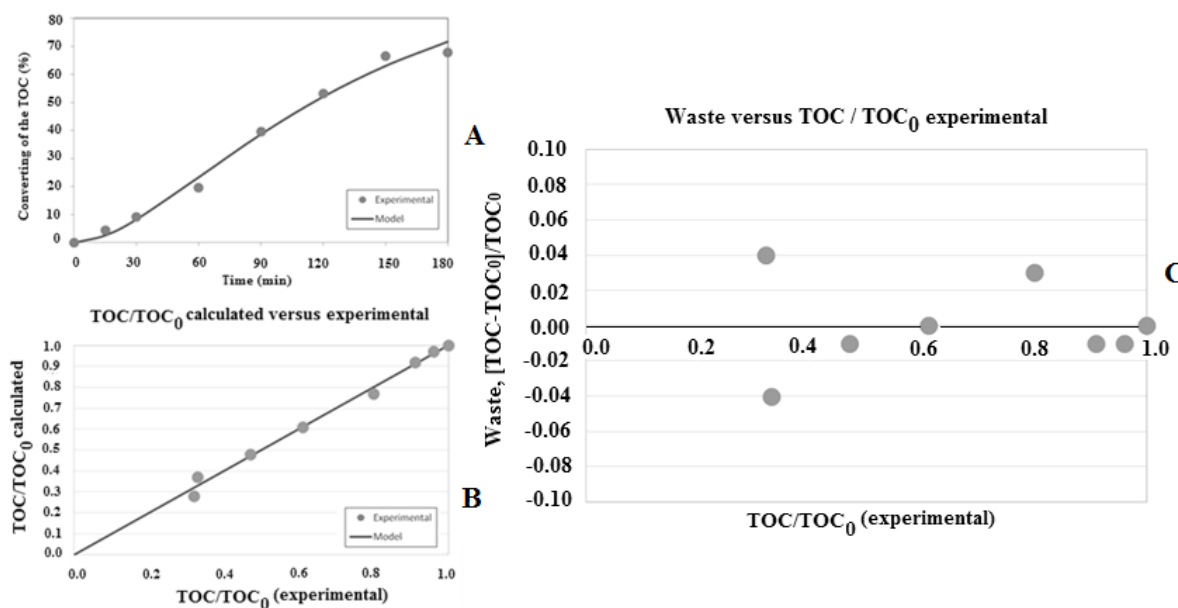| Seed	EBT	Water	EPT1%	EPT5%	EPT10%	**EPT50%**	**EPT70%**	**EPT100%**
Impatiens balsamina	9.67	10.00	9.67	10.00	10.00	10.00	10.00	9.33
Celosia cristata	10.00	9.67	9.67	10.00	9.67	6.33	5.00	0.00
Americano Hard	10.00	9.67	10.00	10.00	10.00	10.00	9.67	9.67

Figure 2- *(a): Adjustment of the grouped kinetic model for the TOC conversion of the effluent from the pharmaceutical WWTP, after being submitted to the photo-Fenton process in a bench reactor. (b): Comparison of the results of the calculated versus the experimental residual fraction (TOC/TOC$_0$). (c): Distribution of the residual versus the experimental (TOC/TOC$_0$).*

Table 7: *Average root growth, RGR and GI (%) of the Americano Hard grain and the Impatiens balsamina and Celosia cristata seeds (threefold trials).*

Effluent Test-solution	Average ± Standard deviation(cm)			RGR/GI(%)		
	Impatiens balsamina	Celosia cristata	Americano Hard	Impatiens balsamina	Celosia cristata	Americano Hard
WATER	8.13± 2.73	6.30± 0.65	3.20± 0.72	1.00/100.00	1.00/100.00	1.00/100.00
EBT	7.83± 1.55	5.67± 0.72	2.60± 1.04	0.96/93.13	0.90/93.02	0.88/91.56
EPT1%	10.30± 1.39	6.12± 0.91	2.60± 1.04	1.27/122.46	0.98/97.88	0.81/84.02
EPT5%	7.60 ± 1.65	1.93 ± 0.76	2.10 ± 0.89	0.93/93.44	0.31/31.73	0.66/67.86
EPT10%	8.97 ± 0.15	1.07 ± 0.11	1.50 ± 0.17	1.10/110.24	0.17/16.93	0.47/48.47
EPT50%	3.97 ± 0.29	0.73 ± 0.11	1.13 ± 0.32	0.49/48.77	0.12/7.62	0.3536.62
EPT70%	2.67 ± 0.55	0.63 ± 0.11	0.83 ± 0.30	0.33/32.79	0.10/5.20	0.26/26.04
EPT100%	1.67 ± 0.06	---	0.90 ± 0.20	0.20/19.12	0.00/0.00	0.2828.12

*EBT = Effluent before the treatment; EPT = Post-treatment effluent

The analysis of Table 7 indicates that, for the higher effluent concentration, the root growth was inhibited on both the seeds and the grain studied. This demonstrates that even though the compounds formed after the AOP did not interfere with the germination, it still caused some disturbance in the development of the species studied. A more thorough analysis was, therefore, carried out to determine the relative growth rate (RGR) and the germination index in percentage GI (%), as can be seen in Table 7 and Figure 3.

Having calculated the RGR and the GI (%) for the three species analysed, it was possible to depict the results obtained on the graph shown in Figure 3.

Figure 3- *Graphic analysis of the RGR and GI(%) for the seeds and grain analysed.*

An analysis of Figure 4 led us to conclude that, the growth of the roots of three species studied was reduced. This reduction was not substancial in the case of the post-treatment effluent with dillutions of up to 10%, particularly in the case of the balsamine seed. However, it is important to note that when effluents are dischared on to receptive bodies, they become diluted, similar to that which occurred in the trial conditions with effluent concentrations lower than 50%. The root growth is, therefore similar to the negative control. It can be concluded that the compounds formed after the AOP and subsequent discharge in the environment do not compromise the growth of the species analysed (balsamine, cockscomb and wheat).
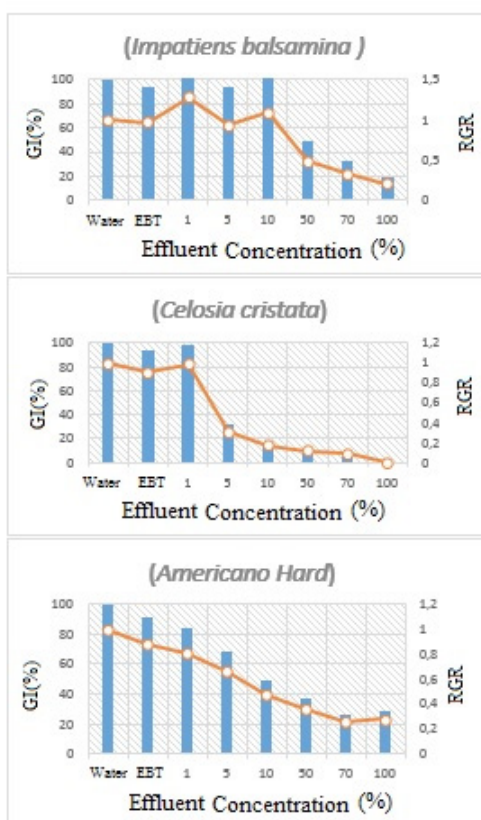
4. CONCLUSION

The use of the photo-Fenton AOP proved to be efficient for the degradation of the pharmaceuticals studied, which were present at the exit of the WWTPs. The degradation percentages attained were 100% for diclofenac and paracetamol, 71.9% for the ASA and 97.6% for dipyrone; the process also proved efficient in the mineralisation of organic matter. The use of the kinetic model made it possible to satisfactorily represent the residual fraction profile of the organic compounds present in the effluent over time (R^2 = 0.992). The toxicity studies, when applied to the samples submitted to the oxidative treatment, showed a lack of toxicity levels, thus justifying the use of the photo-Fenton process for the degradation of these pharmaceuticals.

5. ACKNOWLEDGEMENTS

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