

## Article

# UVC-Assisted Tertiary Treatments for the Removal of Pollutants of Emerging Concern in Real WWTP Matrices

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**Abstract:** The aim of this work is to investigate the enhancement of UVC-based tertiary treatments; for this purpose, real wastewater treatment plant (WWTP) effluent was spiked with a model pollutant, namely acetaminophen. UVC irradiation resulted in some photodegradation of the acetaminophen, which was enhanced upon the addition of hydrogen peroxide (11 mM), but higher amounts of this oxidizing agent resulted in no significant acceleration of the process. An experimental design methodology based on Doehlert matrices showed the significance of hydrogen peroxide concentration and the flow rate for the reactor operating in continuous mode. The addition of low amounts of iron had a positive influence on the process, most probably due to a photo-Fenton-like process using the complexing ability of organic matter. For effluents with higher turbidity, a strategy combining coagulation-flocculation with UVC irradiation was tested: this approach was meaningful as flocculation-coagulation decreased water turbidity and resulted in a more efficient acetaminophen removal. However, under those conditions, the presence of iron did not show a positive role, most probably because of the absence of organic matter, which makes the UVC/H<sub>2</sub>O<sub>2</sub> process more efficient and, on the other hand, humic-like substances available to complex iron to drive a neutral photo-Fenton process.

**Keywords:** acetaminophen; photo-Fenton; UVC irradiation; hydrogen peroxide; tertiary treatment

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## 1. Introduction

One of the major challenges of our society is to ensure universal access to water. Despite this is a ubiquitous substance, not always water where the required quality is available, because of its irregular distribution, pollution, and increasing demands; in this context, the reuse of water is a sustainable alternative to deal with water scarcity [1]. However, in order to avoid threats to human health, more astringent limits for chemical and biological contamination are established in the Regulation (EU) 2020/741 of the European Parliament and European Council on minimum requirements for water reuse [2]. As a consequence of this, improvement of the performance of wastewater treatment plants (WWTP) is a technical and scientific goal to be achieved.

Within WWTP, tertiary processes are designed to enhance the quality of reclaimed water by removing those pollutants reluctant to previous treatments and eliminating potential pathogens [3]. Photochemical processes, chlorination, ozonation, sand filtration, adsorption, or membranes can be used for this purpose [4–9]. Tertiary processes based on irradiation at the Ultraviolet C (UVC) range of the spectrum are among the most widespread systems to conduct disinfection and removal of pollutants of emerging concern at full-scale WWTP due to their effectivity and feasibility [10].

Despite the ability of UVC to photo-oxidize organic pollutants has been widely studied, it is still a hot topic [11]. In some cases, direct photolysis of the pollutants can be achieved [12,13]. However, this process is not always feasible, as the irradiation times are too long or the pollutants do not absorb in the irradiation wavelengths. In this case, UVC has to be combined with other reagents such as hydrogen peroxide, ozone, persulfate, or chlorine, as recently reviewed by Li et al. [14]. Among them, the combination UVC/H<sub>2</sub>O<sub>2</sub> is the most widely implemented at WWTP. However, the UVC and UVC/H<sub>2</sub>O<sub>2</sub> tertiary treatments are not free of problems, such as the high energy consumption of UVC lamps (in most cases based on mercury lamps) is high, as it represents around 20% of the total energy cost of a WWTP and only 30% of which is transformed into UVC radiation [15]. Hence, it is especially interesting to intensify the process by controlled dosing of reagents, determining carefully the effect of sample matrices or coupling pretreatments such as coagulation-flocculation, in order to decrease the amount of organic matter or the turbidity of the effluent.

In the case of UVC/peroxide, the key step is the decomposition of H<sub>2</sub>O<sub>2</sub> into more reactive hydroxyl radicals ( $\cdot$ OH) when irradiated with light whose wavelength is below 300 nm [16], according to equation (1). However, this is not the only potential source of  $\cdot$ OH, as photo-Fenton could also play an important role. This process is based on the ability of iron salts to catalyze the formation of  $\cdot$ OH from H<sub>2</sub>O<sub>2</sub>, which is enhanced by irradiation ( $\lambda < 500$  nm), according to a mechanism that can be summarized by equations (2–3) [17]. The optimum pH value has been considered to be 2.8, which is where the photoactive Fe(OH)<sup>2+</sup> reaches the highest concentration. Despite the implementation of the process at highly acidic pHs is not realistic for tertiary treatment, some papers have been published on its applicability at circumneutral medium to deal with pollutants at low concentration [18–20]. In this context, the presence of dissolved organic matter (DOM) in the effluent might play a significant role, as some organics are able to form a photo-active complex, Fe(DOM), with iron that shifts the optimum pH towards higher values [21–23], according to equation (4). The addition of low amounts of iron (less than 2 mg L<sup>-1</sup>) should not be a serious concern and might greatly enhance the performance of the UVC process. As a matter of fact, significant amounts of dissolved iron can be commonly found in WWTP effluents, as iron salts are added for different purposes such as to remove phosphates as insoluble iron salts or to control H<sub>2</sub>S formation.



However, DOM is known to play diverging roles in photochemical processes as it can enhance the generation of reactive species, but on the other hand, they can produce an inner filter effect, decreasing the amount of photon reaching some parts of the solution and also, acting as a scavenger for the generated reactive species [24]. As coagulation-flocculation is commonly employed to remove macromolecular organic matter, studying the application of this treatment before the photochemical process seems meaningful.

With this background, the aim of this paper is to gain further insight into the applicability of UVC processes as tertiary treatment. For this purpose, the effect of oxygen availability and hydrogen peroxide concentration will be investigated, with a photoreactor operating both in discontinuous and continuous modes. The interaction between flow rate and H<sub>2</sub>O<sub>2</sub> concentration will be determined using experimental design methodology. Finally, the possibility of applying a previous coagulation-flocculation processes will be explored and the UVC-driven photo-Fenton at neutral media will be compared with UV-H<sub>2</sub>O<sub>2</sub> under different scenarios. Acetaminophen has been used as a target pollutant, as it is a widely used anti-inflammatory drug commonly found in the environment [25] and in

WWTP effluents [26]. This compound has been used as a surrogate for pollutants of emerging concern, as it is slightly more reluctant towards oxidative processes than the average of these kinds of contaminants [27].

## 2. Experimental Part

### 2.1. Reagents and Chemicals

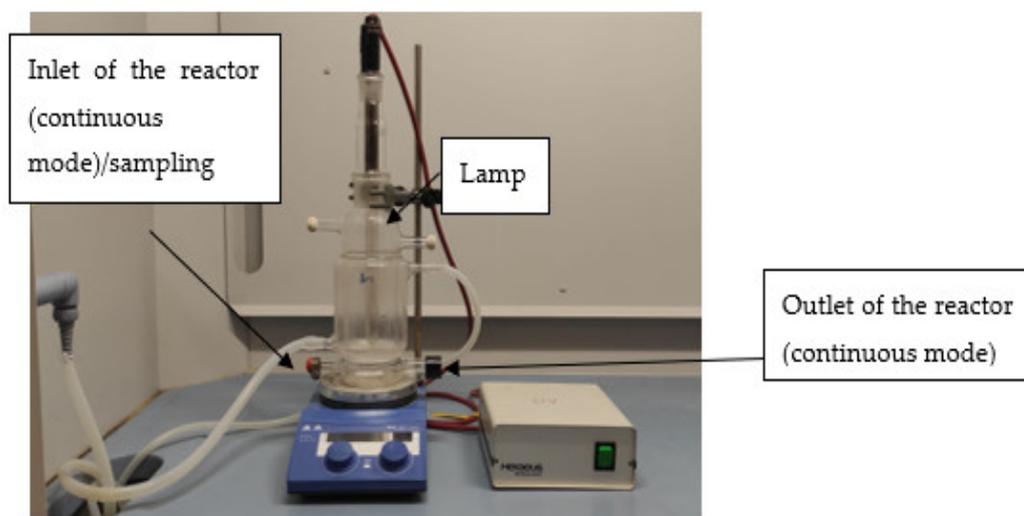
High-purity acetaminophen (<99%) was purchased from Sigma-Aldrich. Sulfuric acid (98%), acetonitrile and methanol (both HPLC grade), iron(II) sulfate heptahydrate, and hydrogen peroxide (33% *w/v*) were obtained from PanReac AppliChem. Ferric sulfate (10 g L<sup>-1</sup>) was used as a coagulant and magnafloc® (0.3 mg L<sup>-1</sup>) was the polyelectrolyte employed as a flocculant. High-purity synthetic air, oxygen, and nitrogen were supplied by Praxair.

Different water matrices were employed to prepare target solutions, namely: a) MilliQ water; b) tap water (pH = 7.9, conductivity = 457 μS cm<sup>-1</sup>, turbidity < 0.3 NTU, DOC < 1 mg L<sup>-1</sup>) and c) water taken from the outlet of a wastewater treatment plant (WWTP) located in the East of Spain. Two different samples of WWTP were employed: WWTP1, which was cleaner (pH = 7.5, conductivity = 1257 μS cm<sup>-1</sup>, turbidity = 11.2 NTU, DOC = 12.3 mg L<sup>-1</sup>) and WWTP2, that has a higher turbidity and organic content (pH = 7.0, conductivity = 1383 μS cm<sup>-1</sup>, turbidity = 41.1 NTU, DOC = 18.3 mg L<sup>-1</sup>).

### 2.2. Reactions

Acetaminophen solutions (1 mg L<sup>-1</sup>; 6.6 mM) were prepared using distilled water, tap water, and WWTP water. In some experiments, hydrogen peroxide (0–107 mM) and/or iron(II) sulfate (0–29 μM; 0–1.6 mg L<sup>-1</sup> of iron) were added. When required, synthetic air, oxygen, or nitrogen were bubbled through the solution.

Irradiations were carried out in a closed glass reactor (8 cm diameter, 25 cm height), a picture of which is given (Figure 1). Different outlets allowed sampling, gas bubbling, and operation in batch or continuous mode. The light source used was a 15 W low-pressure mercury lamp (Heraeus Noblelight) emitting nearly monochromatic irradiation at 254 nm, which was placed axially inside the reactor, protected by a quartz envelope. The system was refrigerated by means of an outer jacket through which water was continuously recirculated. For each experiment, the reactor was loaded with 500 mL of the solution to be treated. Magnetic stirring was kept all along the process. When the system was operated in continuous mode, water was pumped from a reservoir, through the reactor, and then collected in another tank. A peristaltic pump (RESUN) was used; the flow rates were set between 1.84–3.89 L·h<sup>-1</sup>.



**Figure 1.** Experimental set-up employed in this work.

In some experiments, samples were submitted to a previous coagulation-flocculation process. For this purpose, 10 mL of the coagulant was added to 1 L of solution, and the mixture was stirred for 1 min at 120 rpm. Then, the polyelectrolyte was added (10 mL) and stirred at 30 rpm for 5 min. Finally, the solution was kept for 1 h in an Imhoff cone, in order to allow the solids to settle down, and the supernatant was recovered to be submitted to photochemical treatment (Section 3.3).

### 2.3. Chemical Analysis

Samples were taken out from the reactor and flown through polyamide filters (pore diameter of 0.45  $\mu\text{m}$ ), purchased from Macherey-Nagel. In order to avoid further reaction of  $\text{H}_2\text{O}_2$  with the pollutant after sampling, methanol was added in a 2/1 ratio to quench the excess of peroxide.

The concentration of acetaminophen was monitored by high-performance liquid chromatography (Hitachi Chromaster chromatograph; VWR) equipped with a UV/Vis detector. A Prevail Hichrom column (C18-Select; 250  $\times$  4.6 mm; 5  $\mu\text{m}$ ) was employed as stationary phase. The mobile phase consisted of an isocratic mixture of a 1 mM solution of sulfuric acid (40%) and acetonitrile (60%) at a flow rate of 1  $\text{mL}\cdot\text{min}^{-1}$ . Identifications and quantitations were performed by comparison with standards, at a fixed wavelength of 254 nm.

Excitation emission matrices (EEMs) were measured in a Horiba PTI Quanta Master 400 spectrofluorometer, equipped with a Xe arc lamp, employing an excitation range of 250–400 nm (recorded with 5 nm intervals), and emission range from 300 to 600 nm (recorded within 2.5 nm intervals). Absorbance spectra for inner filter effect corrections were measured with a Hitachi-UH5300 spectrophotometer. During the EEM preprocessing, the regions corresponding to the primary Rayleigh scatter were suppressed (white zone in the EEM plots).

### 2.4. Statistical Treatment of Data

An experimental design methodology based on a Doehlert array [28] was employed to evaluate the effect of flow rate (residence time) and hydrogen peroxide amount. For this purpose, a total of 9 experiments,  $k^2+k+1$ , where  $k=2$  (number of analyzed variables), plus two replicates of the central point, were performed (see Table 1 for experimental points). The software Statgraphics Centurion XVI was used for response surface model fitting by means of the least squares method. The percentage of degradation of acetaminophen at the outlet of the reactor working in continuous mode was used as the response surface.

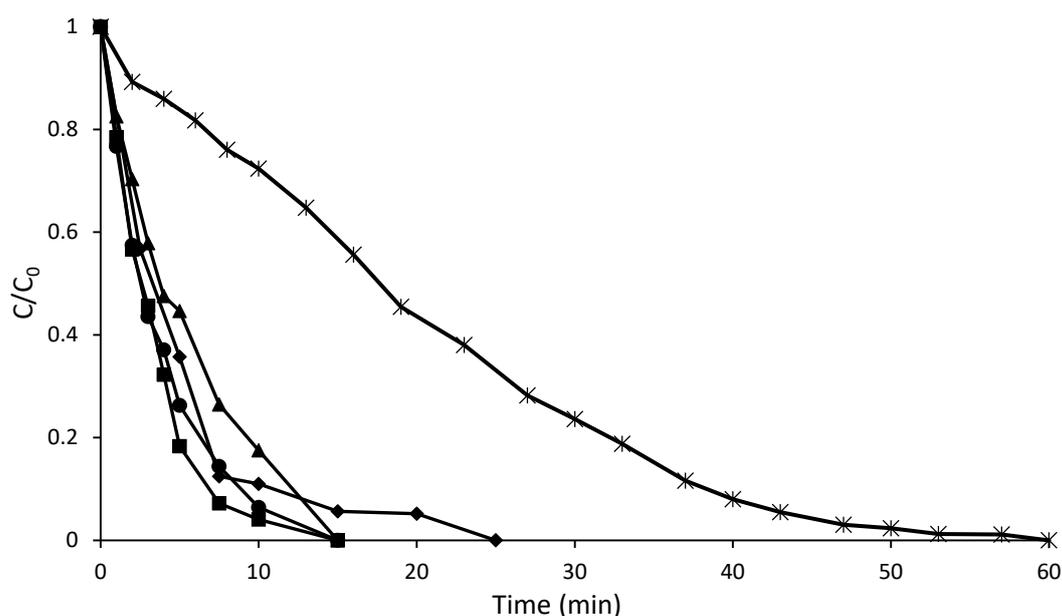
**Table 1.** Experimental points employed for the generation of a surface response based on Doehlert matrices. The hydrogen peroxide concentration and flow rate for each experiment are given, together with the percentage of removal of acetaminophen reached when 4 L of solution were flown through the reactor.

Experiment	[H <sub>2</sub> O <sub>2</sub> ] (mM)	Flow (L·h <sup>-1</sup> )	Degradation (%)
1	1.1	2.9	58.6%
2	2.1	2.9	76.8%
3	1.6	3.9	71.4%
4	0.1	2.9	24.7%
5	0.6	1.8	66.3%
6	1.6	1.8	80.7%
7	0.6	3.9	44.4%
8	1.1	2.9	58.4%
9	1.07	2.9	57.5%

### 3. Results and Discussion

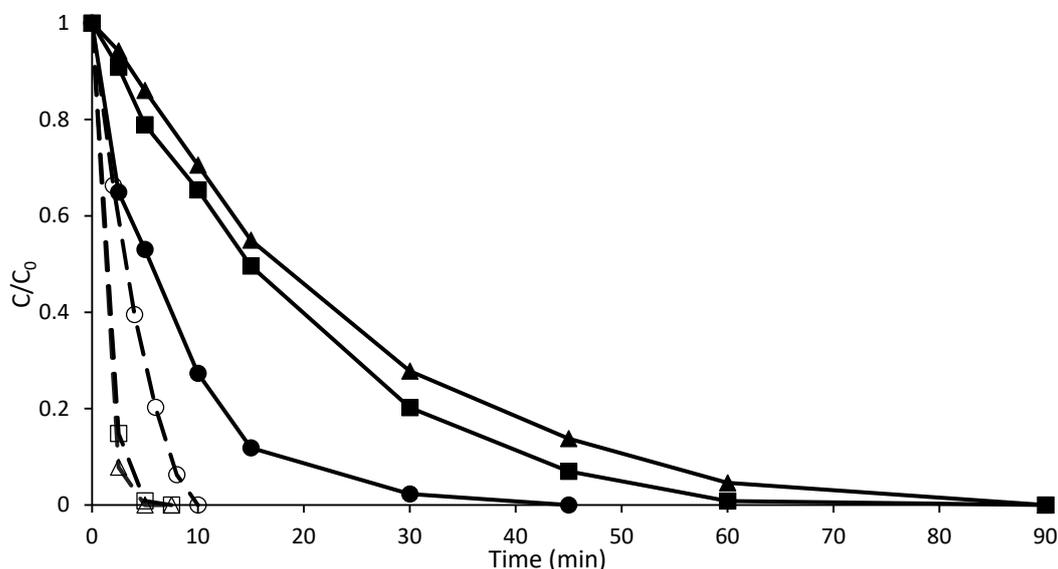
#### 3.1. Photolysis of Acetaminophen

The removal of acetaminophen (1 mg L<sup>-1</sup>) was studied under UVC irradiation in the presence of different amounts of hydrogen peroxide. Figure 2 shows the relative concentration of this compound ( $C/C_0$ , where  $C$  is the concentration at the sampling time and  $C_0$  is the initial concentration of the pollutant) when irradiated with different amounts of hydrogen peroxide (0–107 mM). Although UVC was able to photolyze acetaminophen, it can be observed that H<sub>2</sub>O<sub>2</sub> greatly enhanced its photodegradation, as the time needed to remove completely the pollutant was reduced to less than half when H<sub>2</sub>O<sub>2</sub> was added. This is due to the photolysis of hydrogen peroxide, which generates highly reactive hydroxyl radicals, which are the actual oxidizing species (see introduction, Equation (1)). Once H<sub>2</sub>O<sub>2</sub> is present, the effect of its concentration was not so remarkable in the studied range as, if the sufficient amount of ·OH to ensure efficient degradation of acetaminophen is generated in all cases, higher concentrations of H<sub>2</sub>O<sub>2</sub> results in recombination of these radicals instead of reacting with the acetaminophen molecule [16].



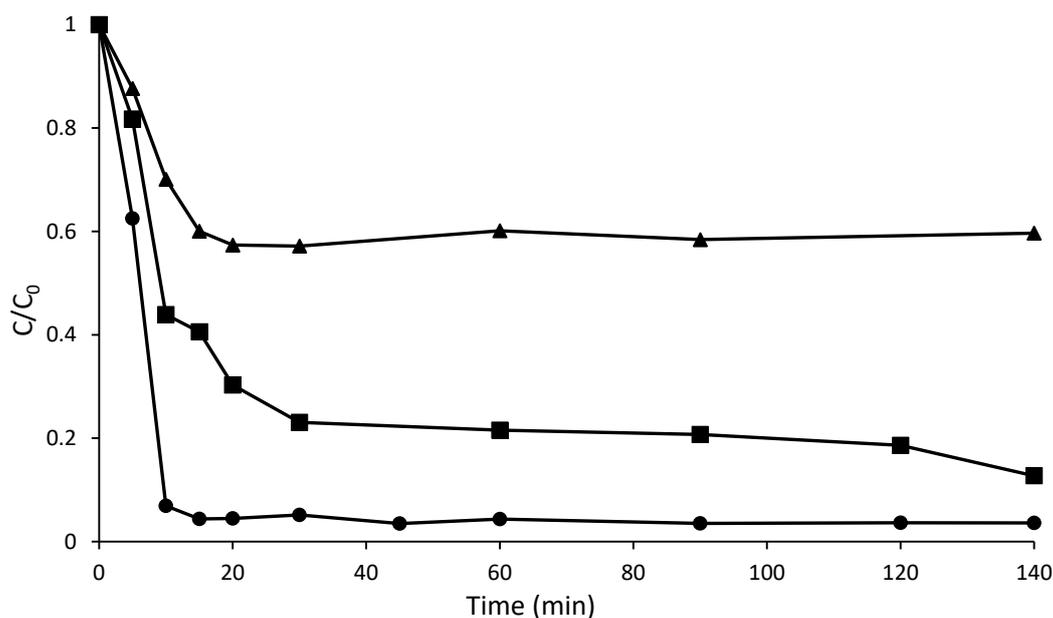
**Figure 2.** Plot of the relative concentration of acetaminophen ( $C/C_0$ , where  $C_0 = 1 \text{ mg L}^{-1}$ ) when irradiated in the presence of a different concentration of H<sub>2</sub>O<sub>2</sub>: 0 mM (X), 11 mM (◆), 21 mM (●), 43 mM (■) and 107 mM (▲).

Experiments were carried out by bubbling oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>) and air, when irradiating with and without H<sub>2</sub>O<sub>2</sub> (Figure 3). In the absence of hydrogen peroxide, the direct photolysis of acetaminophen was faster in the absence of oxygen (bubbling N<sub>2</sub> experiment) than when this gas was present. This might be due to the quenching of the excited states of acetaminophen by the oxygen, which decreases the photolysis rate of this pollutant [29,30]. However, the primary removal of acetaminophen does not guarantee decontamination, and under an N<sub>2</sub> atmosphere, the absence of a final electron acceptor suggests that a strong oxidation of the acetaminophen molecule should be disregarded. On the contrary, when hydrogen peroxide is present, indirect oxidative processes become predominating, following mechanisms involving radical formation (e.g., OH, as stated above). Under these conditions, acetaminophen removal was faster in all cases (complete removal of the pollutant was reached in less than 10 min). In agreement with the indirect photolysis, O<sub>2</sub> played a slightly favorable role, as excited states of acetaminophen are no longer key intermediates, and its presence results in higher availability of oxidizing agents.



**Figure 3.** UVC-driven degradation of acetaminophen in the presence (21 mM) and absence of H<sub>2</sub>O<sub>2</sub> under different atmospheres: air (▲), oxygen (■), nitrogen (●), air/H<sub>2</sub>O<sub>2</sub> (Δ), oxygen/H<sub>2</sub>O<sub>2</sub> (□), nitrogen/H<sub>2</sub>O<sub>2</sub> (○).

The process was also operated in a continuous mode, by pumping the solution containing the pollutants and, eventually, hydrogen peroxide, through the photochemical reactor. A flow rate of 2.74 L·h<sup>-1</sup> was employed, which represented a residence time of 650 s. The amount of solution was 5 L and, when hydrogen peroxide was added, it was dosed in different pulses to reach a final value of 105 mmols (which represented an average concentration of 21 mM). Figure 4 shows the concentration of the pollutant at the outlet of the reactor. The same trends as in the batch mode experiments were observed: UVC was able to reach some removal of acetaminophen (ca. 40%), but the efficiency was greatly enhanced upon the addition of H<sub>2</sub>O<sub>2</sub> (ca. 80%), and when the air was also bubbled in the system, 95% abatement was achieved once the stationary state was reached.



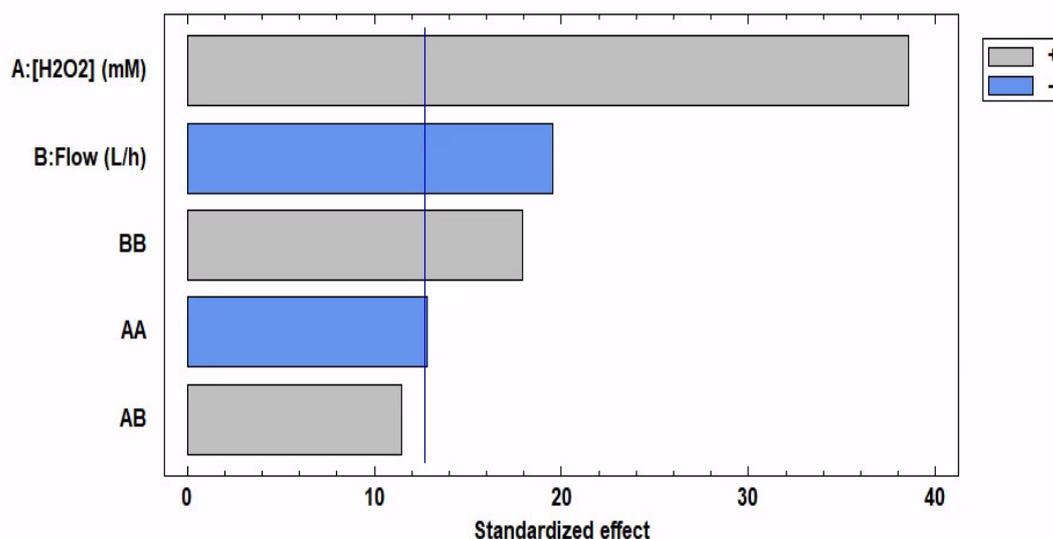
**Figure 4.** Plot of the relative concentration of acetaminophen at the outlet of the reactor when operated in the continuous mode under different conditions: UVC (▲), UVC + H<sub>2</sub>O<sub>2</sub> (21 mM) (■) and UVC + H<sub>2</sub>O<sub>2</sub> (21 mM) + bubbling air (●).

The influence of the concentration of hydrogen peroxide and the flow rate (that in turn determines the residence time and the volumetric energy density) was tested. For this purpose, an experimental design methodology based on Doehlert matrices was employed. The concentration of hydrogen peroxide was decreased by an order of magnitude, as the high percentages of removal reached with 21 mM did not allow for evaluate the effect of these parameters. The experiments that were performed are shown in Table 1, together with the percentage of removal that was obtained at the outlet of the reactor. In order to ensure that the stationary state was reached, samples were taken once 4 L had passed through the reactor.

According to these data, a bi-dimensional response surface was calculated in order to predict the removal of the model pollutant for each experimental condition in the studied domain (see Equation (5)), where [H<sub>2</sub>O<sub>2</sub>] is expressed in mmol·L<sup>-1</sup> and flow rate (Q) in L·h<sup>-1</sup>. The R<sup>2</sup> was 0.9998, which showed that the equation fitted well with the experimental data.

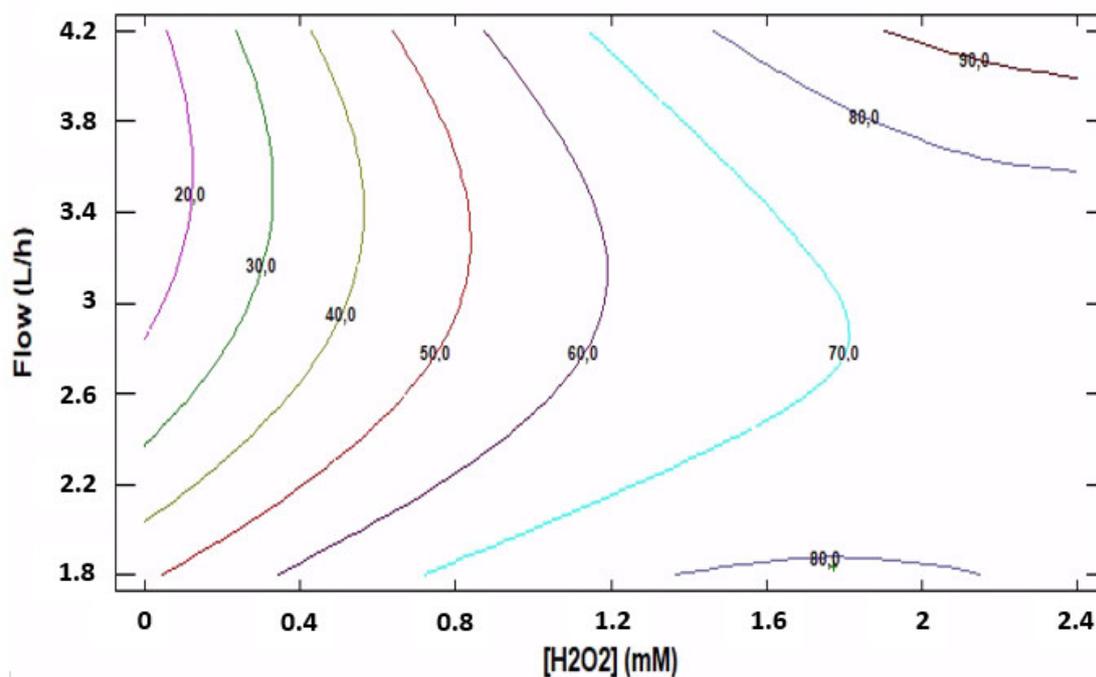
$$\text{Removal (\%)} = 149.4 + 22.2 \cdot [\text{H}_2\text{O}_2] - 74.7 \cdot Q - 10.8 \cdot [\text{H}_2\text{O}_2]^2 + 8.8 \cdot [\text{H}_2\text{O}_2] \cdot Q + 10.6 \cdot Q^2 \quad (5)$$

The Pareto chart shows the standardized effect of each parameter (linear and quadratic coefficients) as well as the interaction among them (Figure 5). It can be observed that the most significant effect can be attributed to [H<sub>2</sub>O<sub>2</sub>] followed by Q. Also, the quadratic coefficients (Q<sup>2</sup> and H<sub>2</sub>O<sub>2</sub> to a lesser extent) were significant. On the contrary, the interaction between both factors ([H<sub>2</sub>O<sub>2</sub>]·Q) was slightly below the threshold of significance.



**Figure 5.** Pareto Chart showing the significance of the studied parameters, their interactions, and the quadratic values. The blue line accounts for the limit of significance

A bi-dimensional plot of the surface response can be found in Figure 6, with the contour lines indicating the percentage of removal that was reached at the outlet of the photoreactor. It can be observed that the increase in the concentration of  $\text{H}_2\text{O}_2$  resulted in an enhancement of the process, although this effect was more remarkable for concentrations below 1.2 mM. Also, the flow rate had some influence, in agreement with the Pareto Chart, decreasing the performance with the increase of this parameter. This can be explained by considering that higher flows resulted in a decrease in the residence time, and in turn, in the irradiation received by the reaction mixture.



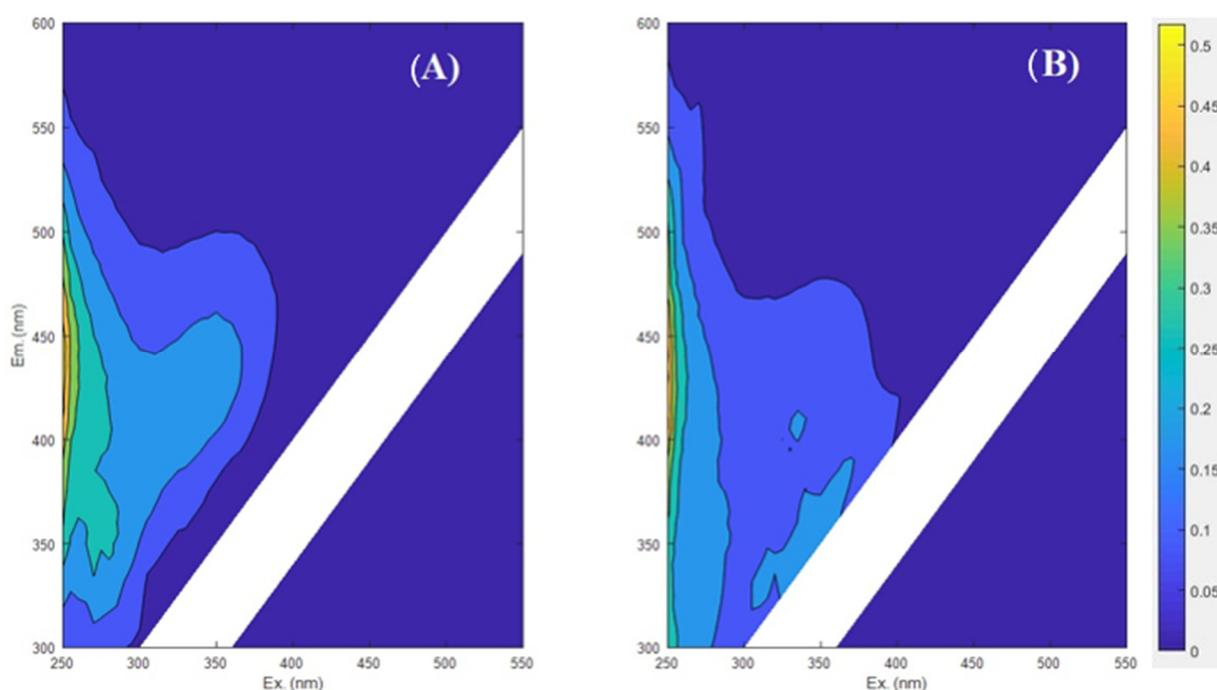
**Figure 6.** Surface response obtained for the removal of acetaminophen in continuous mode. The % of removal at the exit of the reactor is plotted vs. the concentration of  $\text{H}_2\text{O}_2$  and the flow rate.

In order to validate the response surface, an experiment was carried out at an aleatory point within the domain, namely a flow rate of 3 L/h and a concentration of 1.92 mM of

H<sub>2</sub>O<sub>2</sub>. Under those conditions, 75% of removal was predicted, while the real degradation that was obtained was very close to this value, 77%.

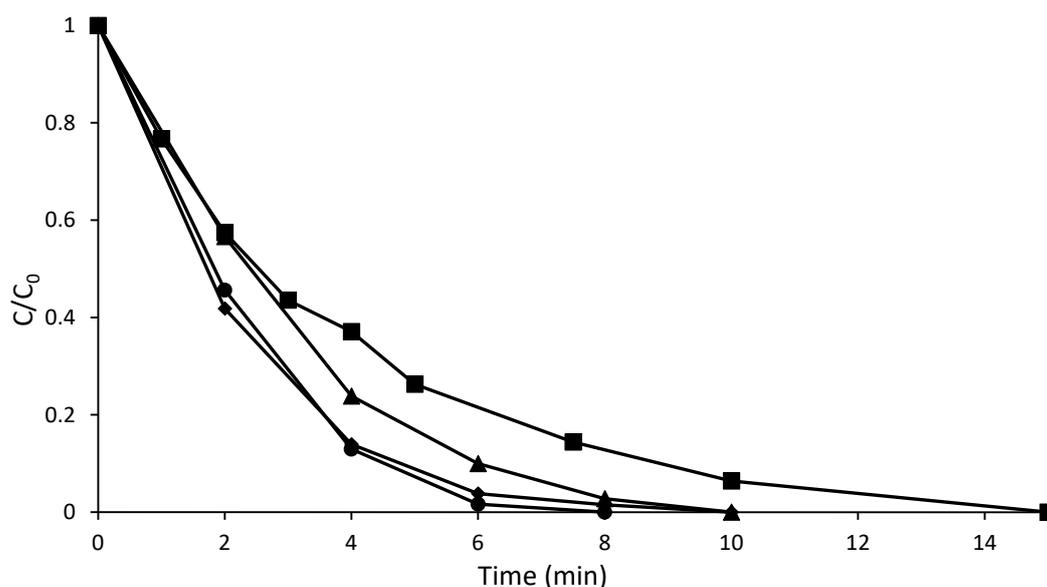
### 3.2. Photo-Fenton Process

The enhancement of acetaminophen degradation in the UV/H<sub>2</sub>O<sub>2</sub> system could be partly attributable to a photo-Fenton-like process, as according to the o-phenantroline method, ca. 0.2 mg L<sup>-1</sup> of iron was present in the WWTP matrix. Although the circumneutral conditions of the solution (pH = 7.2) are very unfavorable for photo-Fenton, because of the formation of inactive iron oxides and hydroxides, small amounts of this metal might remain active, probably complexed by the natural organic matter present in the solution [31]; as a matter of fact, the dissolved organic carbon of the effluent was ca. 17 mg L<sup>-1</sup>. The EEM of effluent shows fingerprints typical of humic substances [32,33] (see Figure 7), which are well known for their ability to form photoactive iron complexes, that have been used to extend the applicability of photo-Fenton towards neutral media [23].



**Figure 7.** Excitation emission matrices were obtained for WWTP1 (A) and c-f-WWTP2 (B).

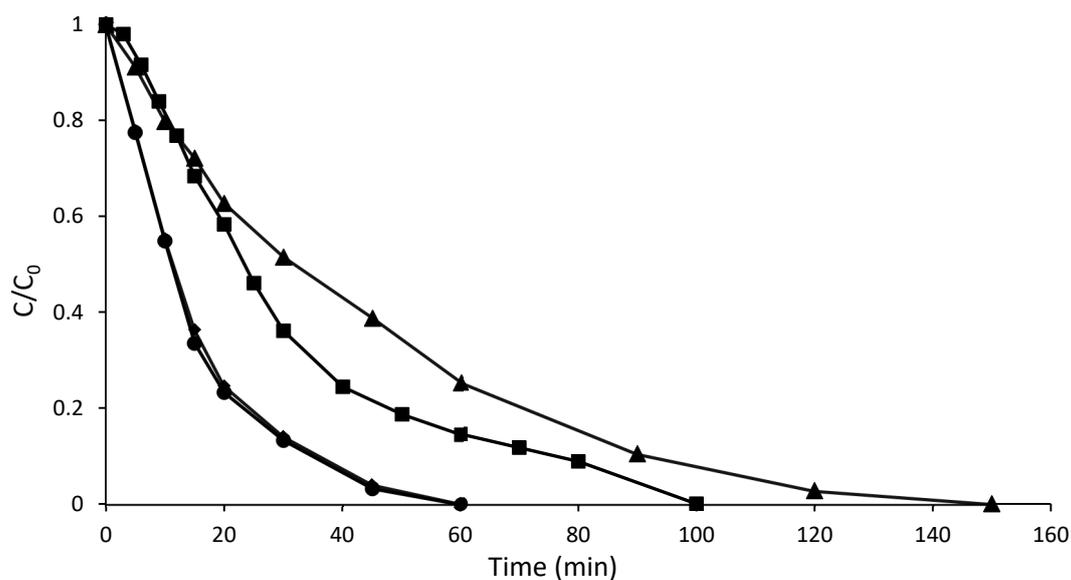
Taking this into account, the addition extra amounts of iron to the effluent might be of interest, as a portion of it could be kept active to drive photo-Fenton-like processes. Figure 8 shows the degradation profile of acetaminophen when different amounts of iron were added to the solution (in the range of 1–5.4  $\mu$ M). It can be observed that the presence of extra amounts of iron resulted in an enhancement of the process, although too high concentrations were detrimental. This indicates that there is a limit in the amount of Fe(II) that can be kept complexed by DOM under those conditions (2.4  $\mu$ M); beyond this point, the decreased efficiency could be attributed to the precipitation of iron(III) oxides and hydroxides, that is faster when the concentration of this species is clearly above the limit of solubility.



**Figure 8.** Influence of photo-Fenton process with WWTP water in discontinuous adding 21 mM of H<sub>2</sub>O<sub>2</sub> without the extra amount of iron (■), adding 1 μM of Fe(II) (◆), 2.4 μM of Fe(II) (●) and 5.4 μM of Fe(II) (▲).

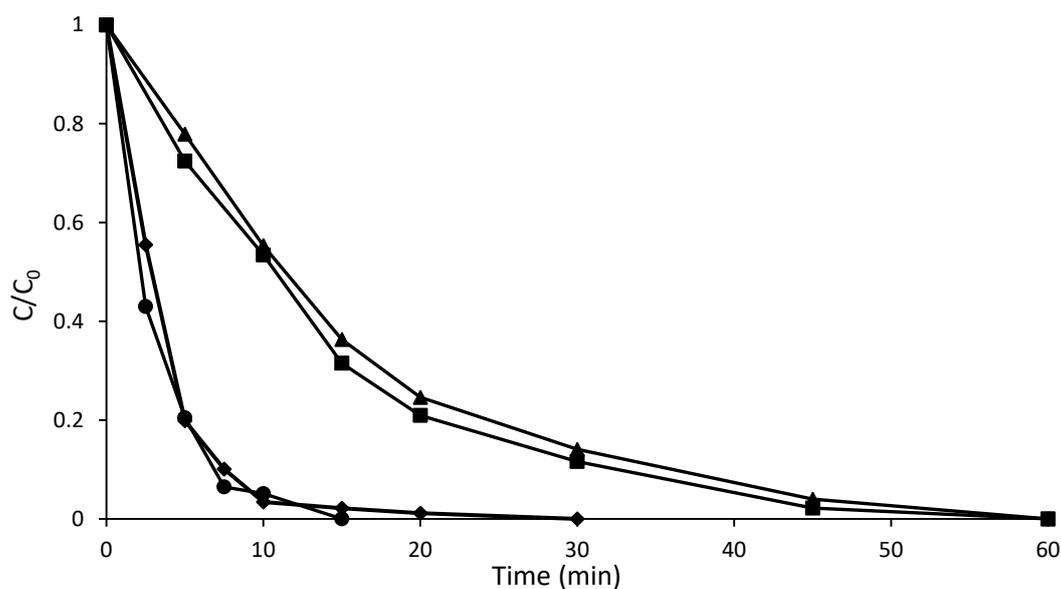
### 3.3. Combination of the Photochemical Processes with Coagulation Flocculation

WWTP2, containing higher turbidity (41.1 NTU) was submitted to a coagulation-flocculation process following the procedure described in Section 2.2. Indeed, coagulation-flocculation followed by photo-Fenton is a train of treatments employed for some highly polluted effluents such as landfill leachate [34,35]. After this treatment, the turbidity decreased to 9.4 NTU, which was closer to the value of the 14.8 NTU measured for WWTP1. Figure 9 shows the plot of the relative concentration of acetaminophen vs. UVC irradiation time using WWTP1, untreated WWTP2, and coagulated-flocculated WWTP2 (c-f-WWTP2). It can be observed that better results were reached with WWTP1 than with raw WWTP2, most probably due to the lower number of photons reaching the pollutants in the second case. However, the best results were obtained with c-f-WWTP2, indicating that a combination of coagulation-flocculation with the photochemical treatment might be useful. Interestingly, coincident results were obtained when acetaminophen was added to WWTP2, then submitted to coagulation-flocculation and finally irradiated, and when the pollutant was added to c-f-WWTP2, indicating that the beneficial effect of coagulation-flocculation is due to the removal of turbidity and organic matter, but it is unable to directly eliminate acetaminophen from the solution.



**Figure 9.** Influence of settleable solids on coagulation-flocculation process using UVC irradiation with acetaminophen 1 mg/L in WWTP2 (▲), WWTP1 (■), c-f-WWTP2 spiked with acetaminophen (◆) and WWTP2 spiked with acetaminophen and submitted to coagulation-flocculation process (●).

The effect of UVC in the presence of  $H_2O_2$  and/or iron salts in c-f-WWTP2 was also investigated. Figure 10 shows that acetaminophen removal was clearly faster in UVC/ $H_2O_2$  than with UVC photolysis; however, in this case, photo-Fenton process showed similar performance to UVC/ $H_2O_2$ . This is in contrast with WWTP1, where some enhancement by photo-Fenton vs. UVC/ $H_2O_2$  was observed. This could be attributed to the low amount of organic matter found in the matrix that (a) resulted in a lower turbidity and hence, in a more efficient photochemical decomposition of  $H_2O_2$  into  $\cdot OH$ , (b) as organic matter can compete with acetaminophen for the generated  $\cdot OH$ , lower organic content resulted in a more efficient attack of  $\cdot OH$  to the pollutant and hence, extra generation of reactive species by photo-Fenton is not required and (c) in the absence of DOM, iron deactivation at circumneutral medium is fast, and hence photo-Fenton is expected to be less efficient. As matter of fact, a comparison between Figure 7A,B shows the disappearance of the signals attributable to humic substances, with the fraction of DOM showing a higher affinity for iron(III).



**Figure 10.** Influence of the photo-Fenton process in c-f-WWTP2 under UVC irradiation (▲), the addition of 0.02 mM of Fe(II) (■), the addition of 21 mM of H<sub>2</sub>O<sub>2</sub> (◆), and the addition of 0.02 mM of Fe(II) and 21 mM of H<sub>2</sub>O<sub>2</sub> (●).

#### 4. Conclusions

The combination of UVC and hydrogen peroxide has been demonstrated to be useful to remove acetaminophen from WWTP effluents. The process depends on oxygen availability, H<sub>2</sub>O<sub>2</sub> concentration as well as flow rate, when the reactor was operated in a continuous mode. For highly turbid effluents, a previous coagulation-flocculation process is useful in order to reach a faster removal of the model pollutant.

The presence of the low amount of iron has been shown to be useful to accelerate the process, most probably due to its complexation by the DOM present in the matrix, in particular humic substances. Thus, the contribution of the photo-Fenton-like process might play an important role, even at the circumneutral pH conditions of the experiments. This effect is more remarkable for high turbidity episodes. However, in scenarios with very low amounts of dissolved organic matter, photo-Fenton-like processes become inefficient and further iron addition does not result in an improvement of UVC/H<sub>2</sub>O<sub>2</sub>. Taking this into account, the possible addition of extra amounts of iron (a few mg·L<sup>-1</sup>) might be convenient when the effluent has a high DOM content, but the reverse is true for effluents with a low concentration of DOM.

Results obtained in this paper indicate that further research is required in order to determine the behavior of other families of pollutants of emerging concern, and also to assess if pathogens removal is reached, as this is another important goal for tertiary processes. Finally, economic studies and life cycle assessment calculations comparing UVC, UVC/H<sub>2</sub>O<sub>2</sub>, and photo-Fenton under different scenarios is an interesting step forward in order to determine which process should be applied.

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