Towards the development of highly-efficient photo-
Fenton processes at neutral pH: the use of a tube-in-
tube membrane microreactor

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Abstract

This work presents a novel approach for developing highly-efficient photo-Fenton processes at neutral pH in continuous operation mode. The system consists of a tube-in-tube membrane microreactor equipped with four lamps as light source and designed for dosing low iron concentrations as catalyst, avoiding the potential iron precipitation. To check its performance, amoxicillin (AMX) was selected as model of organic pollutant (2.00 mg dm$^{-3}$). The process was optimized by studying the influence of hydrogen peroxide concentration (0.00-15.00 mg dm$^{-3}$), light source (UVvis, UVA and UVC), iron concentration (0.00-2.00 mg dm$^{-3}$) and catalyst dosing form (permeation or direct injection) on its removal in synthetic wastewater. A percentage removal higher than 60.00% was attained during the treatment of synthetic wastewater using a Fe$^{2+}$:H$_2$O$_2$ ratio of 1:5 (2.00 mg dm$^{-3}$ Fe$^{2+}$ and 10.00 mg dm$^{-3}$ H$_2$O$_2$) and UVC light irradiation. Then, urban treated wastewater was intensified with AMX (2.00 mg dm$^{-3}$) to study the process efficiency in a real matrix, evaluating the influence of hydrogen peroxide (10.00-80.00 mg dm$^{-3}$), iron concentration (2.00-5.00 mg dm$^{-3}$) and the catalyst dosing form. These tests led to an antibiotic removal of about 45.00%. To reach this removal, optimum iron and hydrogen peroxide concentrations had to be increased up to 5.00 and 40.00 mg dm$^{-3}$, respectively, because the organic matter contained in the real effluent was also oxidized during the process, competing with the antibiotic removal. In comparing the results obtained, the direct injection of catalyst showed a lower AMX removal efficiencies as compared to the permeation attained by this new proposal, being this observation more remarkable during the treatment of real wastewater.

Because of the good antibiotic removal percentages attained in different matrixes, the tube-in-tube membrane microreactor can be considered as a promising system for developing high-efficient photo-Fenton processes at neutral pH.
Keywords: tube-in-tube, photo-Fenton, amoxicillin, advanced oxidation processes

Highlights
- AMX can be removed from real and synthetic wastewater by photo-Fenton at neutral pH.
- A tube-in-tube membrane microreactor guarantees a continuous catalyst dosing for photo-Fenton.
- A Fe^{2+}:H_{2}O_{2} ratio of 1:5 and UVC irradiation improves the process performance.
- Better efficiencies reached with catalyst permeation than direct injection.

1. Introduction.
Nowadays, the presence of organic micropollutants (pharmaceuticals, pesticides, hormones, personal care products…) in wastewater has aroused the interest of scientific
community due to the hazardous associated to this type of compounds, which are not removed by traditional Wastewater Treatment Facilities (WWTFs) [1-4]. For this reason, novel treatment technologies have been developed to ensure their complete abatement, being among them the Advanced Oxidation Processes (AOPs). AOPs are based on the production of large amounts of hydroxyl radicals as oxidizing agent for the removal of organic pollutants [5-8]. These radicals present a higher oxidation power (2.80 V vs. SHE), which significantly contribute to the complete degradation of organics even at low concentrations [9, 10].

One of AOPs that has showed great results in wastewater treatment for the removal of micropollutants is photo-Fenton [11-14]. This technology consists of the massive production of hydroxyl radicals by the Fenton reaction (Eq. 1) and by the irradiation of UVA light (315 < λ < 400) over an iron complex (Fe(HO)_2^+) previously formed during the process (Eq. 2) [12]. Likewise, it is also possible to regenerate the iron catalyst used during photo-Fenton, minimizing the waste production. This fact can also be achieved during single Fenton process (Eqs. 3-4), although the regeneration rate is lower than in photo-Fenton [5].

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad [1] \\
\text{Fe(HO)}_2^+ + \text{hv} & \rightarrow \text{Fe}^{2+} + \cdot \text{OH} \quad [2] \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{H}^+ + \text{Fe(HO)}_2^2+ \quad [3] \\
\text{Fe(HO)}_2^2+ & \rightarrow \text{Fe}^{2+} + \text{HO}_2^\cdot \quad [4]
\end{align*}
\]

One of the main drawbacks of this technology is the experimental conditions required to attain a highly-efficient process. In this context, the pH solution should be maintained at values near 3.0 to ensure a total dissolution of the iron used as catalyst and the generation of large amounts of hydroxyl radicals in wastewater [12, 15]. At higher pH values, iron precipitates as Fe(OH)_3, decreasing the efficiency of Fenton reaction. Therefore, in a real
treatment, it would be required a later neutralization stage to increase the pH up to 6-8 before discharging it into the environment. To avoid this situation, different strategies have been reported to carry out photo-Fenton process at mild pH conditions [16], including:

- The addition of complexing agents: oxalate, citrate, EDTA…[17].
- The controlled dosing of low iron concentrations [18].
- The use of an iron solid catalyst (heterogeneous Fenton) [19].

The dosing of low iron concentrations during photo-Fenton process at neutral pH could be an excellent approach, because it would not only avoid the iron precipitation but also the accumulation of large amounts of metal as final by-products in the treated effluent. For this reason, it is necessary to develop novel systems that allow an efficient addition of low iron concentrations during the process. In this context, the use of a tube-in-tube membrane microreactor can be considered as an alternative for the controlled iron release. This type of reactors has been mainly used for catalytic oxidation processes, which involves reactions between liquid and gas streams due to the improvements in mass transfer [20-22]. Nonetheless, to the authors’ knowledge, it has been never tested for wastewater treatment. Hence, a tube-in-tube membrane microreactor could dose a low homogeneous iron concentration throughout the membrane surface (permeate stream), favoring the mass transfer between iron and hydrogen peroxide for Fenton reaction (Eq. 1). In addition, in these reactors it is very easy the coupling of UV lamps, promoting photo-Fenton processes.

With this background, the present work aims to test a tube-in-tube membrane microreactor for the development of a photo-Fenton process at neutral pH. To do this, distillated water was polluted with amoxicillin (AMX) as model of organic micropollutant. This species has been selected since it is a commonly used antibiotic and
it can be typically found in urban treated wastewater. The influence of the irradiation type
(UVvis, UVA, UVC), iron and hydrogen peroxide concentrations and catalyst dosing
form have been studied in order to fully understand the process, because these parameters
are expected to significantly affect the process performance. Then the process is evaluated
in real wastewater intensified with AMX, in order to extend the conclusion to real
matrixes.

2. Material and methods.

2.1. Chemicals.

Amoxicillin (AMX, C₁₆H₁₉N₃O₅S) was analytical grade and used as received (Sigma
Aldrich, Portugal). Hydrogen peroxide (H₂O₂) used as oxidant was supplied by Fisher
Chemical and iron (II) sulfate heptahydrate (FeSO₄·7H₂O) used as catalyst was supplied
by Panreac. Acetonitrile (Fisher Chemical), methanol (VWR Chemicals) and oxalic acid
2-hydrate (Panreac) HPLC grade were used for the mobile phase to determine the
concentration of antibiotic. Ammonium monovanadate (Merck) was used for the
determination of hydrogen peroxide and, acetic acid (Fisher Chemical), ascorbic acid
(Panreac) and 1,10-phenanthroline-1-hydrate (Panreac) were used for the determination
of iron (II) and total iron. Distillated water was used to prepare synthetic wastewater
polluted with AMX and ultrapure water was used to prepare the mobile phase for HPLC
system.

Urban treated wastewater coming from the secondary clarifier of a WWTF located in
Porto (Portugal) was used for the tests with actual effluents. The main physical-chemical
parameters of wastewater are summarized in Table 1.
### Table 1. Urban treated wastewater composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.27</td>
</tr>
<tr>
<td>Conductivity (µS cm(^{-1}))</td>
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<tr>
<td>Turbidity (NTU)</td>
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<tr>
<td>TOC* (mg dm(^{-3}))</td>
<td>17.00</td>
</tr>
<tr>
<td>TSS** (mg dm(^{-3}))</td>
<td>15.20</td>
</tr>
<tr>
<td>Cl(^-) (mg dm(^{-3}))</td>
<td>94.66</td>
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<tr>
<td>NO(_2^-) (mg dm(^{-3}))</td>
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<tr>
<td>NO(_3^-) (mg dm(^{-3}))</td>
<td>2.79</td>
</tr>
<tr>
<td>SO(_4^{2-}) (mg dm(^{-3}))</td>
<td>47.74</td>
</tr>
<tr>
<td>PO(_4^{3-}) (mg dm(^{-3}))</td>
<td>3.99</td>
</tr>
</tbody>
</table>

*TOC: Total Organic Carbon
**TSS: Total Suspended Solids

#### 2.2. Analytical techniques.

Amoxicillin concentration was measured by chromatography using a Hitachi ELITE LaChrom chromatograph equipped with a DAD detector and a Purospher® RP-18 (5 µm) LiChroCART® 125-4 analytical column. The mobile phase consisted of acetonitrile, methanol and oxalic acid 0.014 M with the following gradient: initially (10:5:85); \( t = 3.0 \) min (15:5:80); \( t = 5.0 \) min (20:5:75); \( t = 7.0 \) min (10:5:85) (flow rate: 0.8 cm\(^3\) min\(^{-1}\)). The DAD detection wavelength was 220 nm, the temperature was kept at 25°C and the injection volume was 20.00 µL. Total Organic Carbon (TOC) was monitored using a TOC-V\(_{\text{CSN}}\) analyzer with an ASI-V autosampler (Shimadzu).
Total iron, iron (II) and hydrogen peroxide concentrations were determined spectrophotometrically using a Spectroquant Prove 300 analyzer (Merck) [23, 24].

2.3. Experimental set-up.

Photo-Fenton process was carried out in a tube-in-tube membrane microreactor that allows a continuously release of a uniform and on-demand dosing of catalyst (Fe$^{2+}$). The reactor is equipped with a ceramic ultrafiltration membrane ($\gamma$-Al$_2$O$_3$) in which the catalyst solution is placed and dosed by using a syringe pump Nexus 6000 (Chemyx Inc.). The membrane is surrounded by a concentric quartz tube with an optical precursor of 0.4 cm which favors a tangential flux. Temperature was kept constant using a thermostatized bath (F12-MA, Julabo) and, the light irradiation (UVvis, UVA or UVC) was provided by four lamps located vicinity the quartz tube with a nominal power of 6.00 W each one. To increase the light intensity in the reactor, the system was closed with an aluminum casing. A detail of the experimental set-up is shown in Figure 1.

Figure 1. Tube-in-tube membrane microreactor for photo-Fenton process.
All experiments were carried out in continuous mode with a catalyst concentration within the range of 0.00-5.00 mg dm$^{-3}$ Fe$^{2+}$ and a hydrogen peroxide concentration within the range 0.00-80.00 mg dm$^{-3}$. Wastewater was continuously fed to the reactor by means of a peristaltic pump (BVP-Z, Ismatec).

3. Results and discussion.

Figure 2a shows the iron concentration permeated through the microporous membrane in the tube-in-tube reactor with the time (continuous mode). The flow rate of the external effluent (distilled water) was 40.00 dm$^3$ h$^{-1}$ and the permeated flow ([Fe$^{2+}$]: 700.00 mg dm$^{-3}$) was 0.12 dm$^3$ h$^{-1}$.

As can be observed, the iron concentration linearly increases during the process until the maximum concentration around 2.00 mg dm$^{-3}$ is achieved. From this value, iron concentration remains constant which reveals that the steady-state has been reached. Hence, an operation time of 4 minutes (residence time: 5.40 seconds) is enough to ensure the permeation of the maximum iron concentration, opening the possibility of developing the photo-Fenton process at neutral pH in continuous mode (the most common operation mode in industrial plants) with the addition of low iron concentrations.

To check this assumption, the removal of antibiotic amoxicillin (2.00 mg dm$^{-3}$) was carried out by photo-Fenton at neutral pH with the Fe$^{2+}$:H$_2$O$_2$ ratio of 1:5 ([Fe$^{2+}$]$_{permeated}$: 2.00 mg dm$^{-3}$; [H$_2$O$_2$]: 10.00 mg dm$^{-3}$) as initial approach [25]. The external effluent consisted of distilled water polluted with 2.00 mg dm$^{-3}$ AMX and hydrogen peroxide (10.00 mg dm$^{-3}$). At this point, it is important to highlight that the chemical oxidation of AMX by hydrogen peroxide was previously checked and, results discarded the possible pollutant removal by the direct contact in the bulk solution. The dynamic behavior of the
system in terms of pollutant removal and hydrogen peroxide consumption is shown in Figure 2b.

Figure 2. (a) Iron (II) permeated through the microporous membrane in the tube-in-tube reactor. (b) Dynamic behavior of the system during the photo-Fenton treatment of synthetic wastewater polluted with AMX. \([\text{Fe}^{2+}]_{\text{permeated}}: 2.00 \text{ mg dm}^{-3}; W_{\text{UVA}}: 24.00 \text{ W (4 x 6.00 W)}; T: 25^\circ\text{C}; Q_{\text{feed}}: 40.00 \text{ dm}^3 \text{ h}^{-1}; Q_{\text{permeation}}: 2.00 \text{ cm}^3 \text{ min}^{-1}. (\blacksquare) \text{AMX}; (\square) \text{H}_2\text{O}_2.\]

The trends observed are similar for both compounds which indicates that the system works properly: there is an initial decrease followed by a plateau zone which corresponds
with the steady-state. The results obtained show that it is possible to achieve an antibiotic
removal percentage of 25.48% during the process. This value is not too high, in particular
when taking into account that the initial AMX concentration was 2.00 mg dm\(^{-3}\). On the
other hand, the residual hydrogen peroxide concentration in the steady-state was around
6.00 mg dm\(^{-3}\) which suggests that it has not been significantly consumed during the
process. However, these results reveal that it is possible to carry out the photo-Fenton
process at neutral pH for the removal of organic micropollutants. For this reason, the
influence of several operation variables has been carried out to improve the pollutant
removal performance.

Figure 3 shows the pollutant removal percentage as function of the initial hydrogen
peroxide concentration during the photo-Fenton process at neutral pH.

Figure 3. Influence of the initial hydrogen peroxide concentration on AMX removal
during the photo-Fenton treatment of synthetic wastewater. [AMX]₀: 2.00 mg dm\(^{-3}\);
[Fe\(^{2+}\)]_{permeated}: 2.00 mg dm\(^{-3}\); \(W_{\text{UVA}}\): 24.00 W (4 x 6.00 W); T: 25°C; \(Q_{\text{feed}}\): 40.00 dm\(^{3}\) h\(^{-1}\);
\(Q_{\text{permeation}}\): 2.00 cm\(^{3}\) min\(^{-1}\).
As can be observed, the antibiotic removal increases with the hydrogen peroxide concentration, reaching a maximum percentage of 33.73 % when working with 15.00 mg dm\textsuperscript{3} H\textsubscript{2}O\textsubscript{2}. At values lower than 10.00 mg dm\textsuperscript{3}, the percentage removal was only around 16.00 % for all the tests carried out which can be due to that Fenton’s reaction (Eq. 1) is less favored stoichiometrically [26] and, hence, the production of free hydroxyl radicals (the main species responsible for antibiotic removal) is lower. In addition, a low concentration of hydrogen peroxide in the system can lead to a less efficient interaction of this oxidant with the iron and, in turn, this could promote a rapid iron precipitation before its reaction, decreasing the process performance.

The higher efficiency for the antibiotic removal during the photo-Fenton process at neutral pH using a tube-in-tube membrane microreactor has been obtained when using 15.00 mg dm\textsuperscript{3} H\textsubscript{2}O\textsubscript{2} as initial concentration. However, an important point that should be taking into consideration is the residual hydrogen peroxide after the treatment. In this case, a 67.40 % of hydrogen peroxide has not been consumed during the process and, it remains in the final effluent. This value is higher than those obtained when working with an initial concentration of 10.00 mg dm\textsuperscript{3} H\textsubscript{2}O\textsubscript{2}. For this reason, it is necessary to establish the optimum value for a significant antibiotic removal and with lower residual products.

Based on the results presented in Figure 3, the influence of other operation variables has been carried out using an initial hydrogen peroxide concentration of 10.00 mg dm\textsuperscript{3} because the residual concentration of this species is lower under these operating conditions and, this value will also decrease the operation costs of the system for the scale-up of the technology.

Figure 4 shows the antibiotic removal percentage as function of the irradiation type during the photo-Fenton process at neutral pH. The permeated iron (II) concentration was 2.00 mg dm\textsuperscript{3} and the initial hydrogen peroxide concentration was 10.00 mg dm\textsuperscript{3}.
Figure 4. Influence of irradiation type on AMX removal during the photo-Fenton treatment of synthetic wastewater. [AMX]₀: 2.00 mg dm⁻³; [Fe²⁺]permeated: 2.00 mg dm⁻³; [H₂O₂]₀: 10.00 mg dm⁻³; T: 25°C; Q feed: 40.00 dm³ h⁻¹; Q permeation: 2.00 cm³ min⁻¹.

The highest antibiotic removal percentage is achieved when using UVC (65.21 %) as light source. Specifically, it is approximately 2.5 times higher than the result obtained with UVA. This behavior is related to the photo-activation of the species present in the effluent when using this irradiation type. In this context, UVA irradiation can only promote the generation of hydroxyl radicals by the activation of iron (Eq. 2) during photo-Fenton process. However, the use of UVC light allows to generate these radicals by the activation of both iron and hydrogen peroxide (Eq. 6) [27, 28]. Hence, the amount of free hydroxyl radicals available for the oxidation of the antibiotic is higher, increasing the process efficiency.

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]  

Another important result that should be highlighted is the removal of AMX during photo-Fenton with UVvis as light source. In this case, the antibiotic removal percentage was
54.22 %, 2 times higher than the value obtained when applying UVA. This is an unexpected behavior, taking into account that UVvis wavelength (400-780 nm) is higher than UVA (315-400 nm) and, therefore, it is expected a lower contribution of UVvis light on organics removal as reported in literature for the treatment of other organics by photo-Fenton process [29]. These results could open the possibility of developing photo-Fenton processes at neutral pH for the removal of micropollutants using a tube-in-tube membrane microreactor with UVvis as irradiation type and, hence, it would be possible to carry out the photo-Fenton process with natural sunlight as light source, decreasing the operating costs. To check this supposition, the spectrum of the UVvis lamp used was measured (data not shown), finding a little absorption in the region of UVA (366 nm). This could explain the better results achieved during the photo-Fenton process with UVvis as light source: a combined effect of UVvis and UVA irradiation types. Therefore, it must be assumed a lower antibiotic removal efficiency if the lamp used only present UVvis irradiation type. Finally, the test carried out without light (dark) shows the lower antibiotic removal percentage, as expected. Under these conditions, the removal of AMX takes mainly place by the production of hydroxyl radicals from Fenton’s reaction (Eq. 1). Consequently, the interactions between iron and hydrogen peroxide plays a key role because there are not photo-activated species that favor the generation of large amounts of hydroxyl radicals in the effluent which contribute to the degradation process.

Figure 5 shows the influence of the permeated iron concentration on AMX removal during the photo-Fenton process at neutral pH using UVC as light source. This has been selected based on the previous results obtained (Figure 4).
Figure 5. Influence of iron concentration on the removal of antibiotic AMX during the photo-Fenton process of synthetic wastewater. $[\text{AMX}]_0$: 2.00 mg dm$^{-3}$; $[\text{H}_2\text{O}_2]_0$: 10.00 mg dm$^{-3}$; $W_{\text{UVC}}$: 24.00 W (4 x 6.00 W); T: 25°C; $Q_{\text{feed}}$: 40.00 dm$^3$ h$^{-1}$; $Q_{\text{permeation}}$: 2.00 cm$^3$ min$^{-1}$.

As can be observed, the process efficiency increases with the iron concentration permeated, reaching a maximum removal percentage of 65.21% when working with 2.00 mg dm$^{-3}$ Fe$^{2+}$. At values lower than 2.00 mg dm$^{-3}$, the process performance was similar for all the tests carried out (percentage removal of 35.00-45.00%) which clearly indicates that higher amounts of catalyst are necessary to improve the photo-Fenton process efficiency in terms of antibiotic removal. At this point, it is important to bearing in mind that the use of iron concentrations higher than 2.00 mg dm$^{-3}$ during photo-Fenton of synthetic wastewater with the proposed system was initially discarded to avoid a possible membrane fouling since the solution inside the membrane that allows to permeate 2.00 mg dm$^{-3}$ Fe$^{2+}$ was very concentrated (700.00 mg dm$^{-3}$).
On the other hand, the absence of iron in the system leads to the development of another AOP: UVC/H\textsubscript{2}O\textsubscript{2} oxidation. This technology is mainly based on the production of free hydroxyl radicals as oxidant species for organic matter removal by the photo-activation of H\textsubscript{2}O\textsubscript{2} (Eq. 6) [30]. Results shown in Figure 5 indicate that it is possible to attain an antibiotic removal of 41.22 % when working without iron in the tube-in-tube membrane microreactor. This fact reveals that there is a negligible contribution of Fenton process on the antibiotic removal when working with iron concentrations within the range 0.10-1.00 mg dm\textsuperscript{-3} since the removal percentage was similar than that obtained during UVC/H\textsubscript{2}O\textsubscript{2} process (0.00 mg dm\textsuperscript{-3} Fe\textsuperscript{2+}). Hence, it seems necessary to carry out the photo-Fenton process for the removal of antibiotic AMX with an Fe\textsuperscript{2+}:H\textsubscript{2}O\textsubscript{2} ratio of 1:5 to observe a significant influence of the Fenton´s chemistry, being 2.00 mg dm\textsuperscript{-3} the iron concentration permeated. For this reason, it can be assumed that the first approach proposed to develop the photo-Fenton process for the removal of AMX using the tube-in-tube membrane microreactor ([Fe\textsuperscript{2+}]: 2.00 mg dm\textsuperscript{-3}; [H\textsubscript{2}O\textsubscript{2}]: 10.00 mg dm\textsuperscript{-3}) was appropriate.

Photo-Fenton process at neutral pH using a tube-in-tube membrane microreactor with UVC light for the dosing of low iron concentrations has allowed to attain antibiotic removal percentages higher than 60.00 %, working in continuous mode and with a low residence time. This is an excellent and promising result, taking into account that most of the papers reported in literature for the removal of organic micropollutants by photo-Fenton are carried out at acidic pH to ensure the iron dissolution [5, 15, 31], requiring a neutralization post-treatment which increases the operating costs. However, to assess the advantages of this technology, it is necessary to compare the results obtained with another system where low iron concentrations are directly injected to the effluent containing hydrogen peroxide (conventional photo-Fenton process). To do this, the reaction system was modified, including an additional valve that allow to carry out the photo-Fenton
process at neutral pH by direct injection of the catalyst (Fe$^{2+}$). Different experiments were performed, varying the iron concentration injected and, the results are shown in Figure 6.

**Figure 6.** Influence of catalyst injection type on the removal of antibiotic AMX during the photo-Fenton process of synthetic wastewater. [AMX]$_0$: 2.00 mg dm$^{-3}$; [H$_2$O$_2$]$_0$: 10.00 mg dm$^{-3}$; W$_{UVC}$: 24.00 W (4 x 6.00 W); T: 25ºC; Q$_{\text{feed}}$: 40.00 dm$^3$ h$^{-1}$; Q$_{\text{permeation}}$: 2.00 cm$^3$ min$^{-1}$. (■) catalyst permeated; (□) catalyst directly injected.

As expected, the antibiotic removal percentage increases with the iron concentration, regardless the catalyst dosing mode: permeation or direct injection. However, it can be clearly seen that the iron permeation leads to higher efficiencies than those obtained when iron is directly injected in the system for all the tests carried out. Specifically, the removal of AMX by using the tube-in-tube membrane microreactor with iron permeation was a 23.22, 19.25 and 20.65 % higher than the results obtained when working with direct injection for 0.10, 0.50 and 2.00 mg dm$^{-3}$ Fe$^{2+}$, respectively. Likewise, it should be noted that the antibiotic removal during the direct injection with the higher iron concentration (2.00 mg dm$^{-3}$) was also lower than the value obtained when working with iron
permeation and 0.50 mg dm$^{-3}$ Fe$^{2+}$ (44.56 vs. 45.32 %). This highlights the higher efficiency of the iron permeation as catalyst dosing for the removal of AMX, even with very low iron concentrations. The different behavior between both catalyst dosing modes can be related to a rapid iron precipitation during the process. In this context, the direct injection takes place at the entrance of the reactor, increasing the contact time between the iron solution and the synthetic effluent polluted with AMX before the tube-in-tube membrane microreactor. This can promote the rapid iron precipitation and, therefore, a lower antibiotic removal efficiency. Opposite to that, the iron permeation through the membrane surface guarantees a homogeneous iron concentration along the reactor, improving the mass transfer for photo-Fenton process before the possible iron precipitation at neutral pH. These results clearly demonstrate that the use of a tube-in-tube membrane microreactor for the dosing of low iron concentrations by permeation allows to carry out high-efficient photo-Fenton processes at neutral pH for the removal of organic pollutants.

Once the proposed reactor has been proven efficient for the removal of antibiotic AMX in synthetic wastewater and the process has been completely optimized, the treatment of actual wastewater coming from the secondary clarifier of an urban WWTF was performed. The effluent was intensified with 2.00 mg dm$^{-3}$ AMX and, the photo-Fenton process was carried out with different iron (2.00-5.00 mg dm$^{-3}$) and hydrogen peroxide (10.00-80.00 mg dm$^{-3}$) concentrations. Figure 7 shows the influence of the hydrogen peroxide concentration on AMX and TOC removal during the photo-Fenton process using 2.00 (Figure 7a) and 5.00 (Figure 7b) mg dm$^{-3}$ Fe as catalyst.
Figure 7. Influence of hydrogen peroxide concentration on the removal of antibiotic AMX and TOC during the photo-Fenton process of urban treated wastewater. [AMX]₀: 2.00 mg dm⁻³; \( W_{UVC} \): 24.00 W (4 x 6.00 W); T: 25°C; \( Q_{\text{feed}} \): 40.00 dm³ h⁻¹; \( Q_{\text{permeation}} \): 2.00 cm³ min⁻¹. (■) AMX; (□) TOC. (a) \([\text{Fe}^{2+}]_{\text{permeated}}\): 2.00 mg dm⁻³; (b) \([\text{Fe}^{2+}]_{\text{permeated}}\): 5.00 mg dm⁻³.

The use of 2.00 mg dm⁻³ \( \text{Fe}^{2+} \) as catalyst leads to antibiotic removal percentages around 10.00 % (Figure 7a). These values are lower than those obtained during the treatment of
synthetic wastewater even increasing the hydrogen peroxide concentration up to 40.00 mg dm\(^{-3}\) and, it is directly related to the different water matrix. In this context, urban treated wastewater present organic and inorganic species in its composition which can react with the hydroxyl radicals produced, decreasing the process efficiency for antibiotic removal \[32\]. Hence, there can be a competitive oxidation between the natural species present in the real effluent and AMX that significantly influences the process performance. Regarding the mineralization of the organic matter, TOC results show a very low removal percentage, reaching a null depletion when using 40.00 mg dm\(^{-3}\) H\(_2\)O\(_2\). This suggests that natural organic matter contained in the effluent requires large amounts of hydroxyl radicals for its total oxidation to carbon dioxide. For this reason, the iron and hydrogen peroxide concentrations were increased up to 5.00 and 80.00 mg dm\(^{-3}\), respectively, to check if it is possible to increase the process efficiency in terms of antibiotic and TOC removal (Figure 7b). Prior to these experiments, the permeation of 5.00 mg dm\(^{-3}\) Fe\(^{2+}\) was carried out using a synthetic wastewater polluted with 2.00 mg dm\(^{-3}\) AMX and 40.00 mg dm\(^{-3}\) H\(_2\)O\(_2\) to check the possible membrane fouling. An antibiotic removal percentage of 80.56 % was attained during this test, indicating that it was possible to operate with a permeate concentration of 5.00 mg dm\(^{-3}\) Fe\(^{2+}\) without decreasing the membrane efficiency by fouling.

Results plotted in Figure 7b show that hydrogen peroxide concentrations higher than 40.00 mg dm\(^{-3}\) are required to attain an antibiotic removal percentage around 45.00 % when using 5.00 mg dm\(^{-3}\) Fe\(^{2+}\) as catalyst. This value is more similar than those obtained during the treatment of synthetic wastewater (65.21 %) and, therefore, it indicates that higher concentrations of iron and hydrogen peroxide are necessary to ensure an efficient photo-Fenton process for the removal of AMX. Furthermore, data obtained confirm that the oxidants produced during the treatment of real wastewater are not only wasted on
antibiotic removal but also on the oxidation of other species contained in the effluent.

Nonetheless, if hydrogen peroxide concentration is very high (80.00 mg dm\(^{-3}\)), there is not a significant improvement in AMX removal. Under these conditions, the residual hydrogen peroxide concentration was around 70.00 % which suggests that this higher concentration does not favor the photo-Fenton process. Likewise, at values of 20.00 mg dm\(^{-3}\) \(\text{H}_2\text{O}_2\), the AMX removal was very low (15.84 %), pointing out that this ratio \(\text{Fe}^{2+}:\text{H}_2\text{O}_2\) is not suitable for carrying out the treatment of real wastewater polluted with AMX by photo-Fenton at neutral pH. On the other hand, the mineralization efficiency increases with the hydrogen peroxide concentration, reaching a maximum removal percentage of 10.39 % when using 80.00 mg dm\(^{-3}\) \(\text{H}_2\text{O}_2\) and 5.00 mg dm\(^{-3}\) \(\text{Fe}^{2+}\). At this point, it is important to highlight that it was not possible to mineralize the organic matter present in the effluent using 2.00 mg dm\(^{-3}\) \(\text{Fe}^{2+}\) as catalyst (Figure 7a). This fact confirms, once again, the need of high concentration of iron and hydrogen peroxide to attain an efficient organic matter removal in real wastewater by photo-Fenton at neutral pH with a tube-in-tube membrane microreactor.

Finally, the direct injection of the catalyst was also studied during the treatment of real wastewater polluted with AMX to check the robustness of the proposed system, taking into account the previous results obtained with synthetic wastewater (Figure 6). Figure 8 shows the removal percentage of AMX and TOC during the photo-Fenton treatment of real wastewater using different catalyst dosing forms.

As can be observed, the direct injection of iron leads to an antibiotic and TOC removal percentages of 13.17 and 6.36 %, respectively. These values are lower than the results obtained when iron is permeated through the membrane and, as previously commented, it is related to the rapid iron precipitation and to the low mass transfer between hydrogen peroxide and the catalyst when working with direct iron injection. Specifically, the
removal of AMX during photo-Fenton with iron permeation is 3.4 times higher than the result obtained when working with direct injection (45.29 vs. 13.17 %). In addition, the mineralization process efficiency is 1.3 times higher with the iron permeation (8.38 vs. 6.36 %). As expected, TOC depletion is lower than the antibiotic removal, which indicates that higher concentrations of free hydroxyl radicals are required to ensure a complete mineralization of the organic matter present in the effluent. Nonetheless, the results obtained during the treatment of real wastewater by photo-Fenton using a tube-in-tube membrane microreactor reveal the robustness of the proposed system and, hence, that it would be possible to develop highly-efficient photo-Fenton processes at neutral pH in continuous mode by the dosing of low iron concentrations for the removal of micropollutants, regardless the wastewater matrix.

**Figure 8.** Influence of dosing iron (II) mode on the removal of antibiotic AMX and TOC during the photo-Fenton process. $[\text{AMX}]_0$: 2.00 mg dm$^{-3}$; $[\text{Fe}^{2+}]$: 5.00 mg dm$^{-3}$; $[\text{H}_2\text{O}_2]_0$: 40.00 mg dm$^{-3}$; $W_{\text{UVC}}$: 24.00 W (4 x 6.00 W); T: 25°C; $Q_{\text{feed}}$: 40.00 dm$^3$ h$^{-1}$; $Q_{\text{permeation}}$: 2.00 cm$^3$ min$^{-1}$. (■) AMX; (□) TOC.

From this work, the following conclusions can be drawn:

- The use of a tube-in-tube membrane microreactor allows to carry out high-efficient photo-Fenton processes at neutral pH in continuous operating mode. Low concentrations of iron (II) are permeated through the membrane, ensuring a constant dosing of catalyst along the reactor and minimizes the precipitation process.

- The removal of antibiotic AMX is significantly improved with a Fe$^{2+}$:H$_2$O$_2$ ratio of 1:5 and using UVC as light source due to the photo-activation of hydrogen peroxide, that favors the production of large amounts of hydroxyl radicals in the effluent. Higher concentrations of hydrogen peroxide generate a less efficient treatment because this species does not completely react during the treatment, resulting a higher residual concentration. With 2.00 mg dm$^{-3}$ Fe$^{2+}$, 10.00 mg dm$^{-3}$ H$_2$O$_2$ and UVC irradiation, it is possible to attain removal percentages higher than 60.00 % with very low residence times.

- Lower antibiotic removal efficiencies than 20.00 % can be obtained when the catalyst is directly injected in comparison with the results obtained by permeation. This points out the potential applicability of the tube-in-tube membrane microreactor for developing efficient photo-Fenton processes at neutral pH.

- The treatment of urban treated wastewater polluted with AMX requires higher concentrations of catalyst and hydrogen peroxide to attain a significant antibiotic removal percentage, because the oxidation of organic matter naturally contained in real effluents competes with the degradation of the organic pollutant. The use
of 5.00 mg dm\(^{-3}\) Fe\(^{2+}\) and 40.00 mg dm\(^{-3}\) H\(_2\)O\(_2\) with UVC irradiation leads to an antibiotic removal percentage around 45.00% in real wastewater.

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