Comparative Study on UV-AOPs for Efficient Continuous Flow Removal of 4-tert-Butylphenol

Saule Mergenbayeva and Stavros G. Poulopoulos

Abstract: In the present study, UV-light-driven advanced oxidation processes (AOPs) have been employed for the degradation of 4-tert-Butylphenol (4-t-BP) in water under continuous flow conditions. The effects of varying space time (10, 20, 40, 60 and 120 min) and oxidant dosage (88.3 mg/L, 176.6 mg/L and 264 mg/L) were examined. 4-t-BP degradation efficiency in the UV-induced AOPs followed the order of UV/H$_2$O$_2$ (264.9 mg/L) ≈ UV/Fe$^{3+}$/H$_2$O$_2$ > UV/Fe$^{3+}$/H$_2$O$_2$ > UV/H$_2$O$_2$ (176.6 mg/L) > UV/H$_2$O$_2$ (88.3 mg/L) > UV/Fe-TiO$_2$ > UV/TiO$_2$ > UV, while UV/Fe$^{3+}$/H$_2$O$_2$ was the most efficient process in terms of Total Organic Carbon (TOC) removal (at the space time of 60 min) among those tested. The combination of UV with 88.3 mg/L H$_2$O$_2$ enhanced pollutant removal from 51.29% to 93.34% after 10 min of irradiation. The presence of H$_2$O$_2$ contributed to the highest 4-t-BP and TOC removal values. Interestingly, the increase in space time from 20 to 60 min resulted in surpassing of the activity of the Fe-TiO$_2$ over commercial TiO$_2$, although it had an almost negligible positive impact on the performance of the UV/H$_2$O$_2$ system as well as H$_2$O$_2$ concentration. The results obtained showed that more than 80% of 4-t-BP could be successfully degraded by both heterogeneous and homogeneous AOPs after 60 min.

Keywords: UV-based advanced oxidation processes; continuous flow; 4-tert-Butylphenol; degradation

1. Introduction

The contamination of water with various chemical compounds found in various types of water bodies [1–3] at low concentrations [4] has attracted increasing attention. These compounds have been termed as emerging pollutants (EPs) and include persistent organic compounds such as pharmaceuticals, personal care products (PCPs), and endocrine disruptive compounds (EDCs) with a high potential of bioaccumulation [5].

Among these pollutants, EDCs constitute a family of organic compounds that affect natural hormones [6]. Their widespread use has led to their release and accumulation in the aquatic environment [7,8]. For example, 4-tert-Butylphenol (4-t-BP), a representative of EDCs [9–12], has been detected in wastewater effluents and surface waters [6,13]. 4-t-BP is an alkylphenol used for the production of phenolic, polycarbonate, and epoxy resins [6]. Though detected at low concentrations in the environment, its ability to bind to the estrogen receptor [14] could result in serious damages for aquatic ecosystems and living organisms [15,16]. Due to its estrogenic activity [10], 4-t-BP has been included by the European Commission in the list of chemicals of very high concern since 2019 [17]. Thus, its toxicity [18,19] and persistence [20,21] impose the elimination of 4-t-BP in water.

Relatively few studies have been conducted to remove 4-t-BP from the aqueous environment; biodegradation and photochemical treatments have been applied mostly. However, biodegradation is not effective since long treatment times are necessary for the complete decomposition of 4-t-BP [22–24]. For instance, the presence of Spirodela polyrrhiza duckweed in environmental water samples led to 4-t-BP removals up to 56% in a 3-day cycle at 28 °C [25].
AOPs are attractive alternatives due to their low cost and environmentally friendly nature. The oxidation efficiency of these processes relies on the generation of highly reactive species such as hydroxyl radicals that have the capacity to degrade and mineralize recalcitrant organic pollutants [26–28]. Among them, UV/H2O2, photo-Fenton, photo-Fenton-like, and heterogeneous photocatalytic processes are gaining increasing popularity [12,13,29,30]. For instance, 4-t-BP at the concentration of 0.1 mM in water was almost completely removed within 50 min by UV/H2O2 [12]. Xiao et al. [31] studied the treatment of 4-t-BP under visible light heterogeneous photocatalysis, and achieved a 95% TOC reduction after 120 min.

Although a substantial amount of research has demonstrated the effectiveness of UV-induced AOPs in the removal of traditional hazardous compounds and many of emerging concern in water, most studies have been conducted in batch systems. The experimental comparison of low power 280 nm UV-photolysis, UV/H2O2 and UV/TiO2 towards the degradation of 1H-benzotriazole demonstrated the superior performance of the UV/TiO2 system in terms of degradation and mineralization [32]. Peternel et al. [33] reported about 2.5 higher mineralization efficiency for the photo-Fenton process compared with the UV/TiO2 system for the organic reactive dye degradation in aqueous solution under 254 nm irradiation. Similarly, Martinez-Costa et al. [34] compared the performance of photo-Fenton processes and UV/H2O2 for the removal of the antibiotics sulfamethoxazole (SMX) and trimethoprim (TMP) in aqueous solution. It was found that UV/H2O2 was beneficial towards the mineralization of organic pollutant than photo-Fenton processes. Despite their promising results, lab scale batch experiments have the disadvantage of low efficiency for treating high volumes of polluted water [35]. In contrast, continuous flow systems appear to overcome such obstacles [36,37]. Silva et al. [38] studied photocatalytic degradation of SMX under simulated solar light in ultrapure water and environmental water matrices (fresh, estuarine and STP effluent). The results showed a sharp decrease in the irradiation time required for the removal of SMX under continuous flow conditions as compared with batch. Shojaeimehr et al. [39] assessed the photocatalytic degradation of diclofenac using porous carbon nitride (mp-CN) immobilized onto stainless steel (SS) plates and determined the optimum operating conditions, including catalyst loading, irradiation source and initial pollutant concentration. They concluded that the combination of continuous flow mode with the immobilized photocatalyst particles could be a promising alternative for treating contaminated water. Senthilnathan and Philip and Vishnuganth et al. [40] have also reported the effective light-driven pesticide removal using heterogeneous catalysts, N-doped TiO2 and granular activated carbon-supported titanium dioxide (GAC-TiO2), respectively.

In the present study, the efficiency of UV-light-driven AOPs (UV/H2O2, UV/Fet2+/H2O2 and UV/Fet3+/H2O2, UV/TiO2 and UV/Fet-TiO2) in terms of 4-t-BP degradation and total organic carbon removal was comparatively investigated under continuous flow conditions. To the best of our knowledge, this is the first study concerning the use of light-driven AOPs in continuous flow for the treatment of 4-t-BP in water by means of homogeneous and heterogeneous processes.

2. Materials and Methods
2.1. Chemicals and Materials
4-t-BP (99%), TiO2-P25 (21 nm particle size, ≥99.5%), FeCl2 (98%), FeSO4·7H2O (≥99.0%), Fe(NO3)3·9H2O (≥98.0%) and methanol (MeOH) of HPLC grade were obtained from Sigma Aldrich. H2O2 (37.6% w/w) was obtained from Skat-Reactiv Company (Almaty, Kazakhstan). Fe-doped TiO2 powders (Fe-TiO2) were synthesized by the wet impregnation method with a 4% Fe:TiO2 molar ratio [21]. Ultrapure water (resistivity 18.2 mΩ cm, Millipore) was used to prepare all solutions.
2.2. Experimental Procedures

A 1000 mL stock solution was prepared by dissolving 30 mg of 4-t-BP in ultrapure water. Depending on the system, H$_2$O$_2$, iron, TiO$_2$ or Fe-TiO$_2$ were added directly to the 4-t-BP solution before being exposed to UV light. The solution was kept under constant stirring using a digital ceramic top hotplate stirrer (Mettler Toledo). In UV/H$_2$O$_2$ processes, three different concentrations of H$_2$O$_2$ (88.3 mg/L, 176.6 mg/L and 264.9 mg/L) were used, while 5 mg/L of iron (Fe$^{2+}$ or Fe$^{3+}$) was added in photo-Fenton and photo-Fenton-like processes. In UV/TiO$_2$ and UV/Fe-TiO$_2$ processes, 200 mg/L of catalyst was tested.

The experiments on the degradation of 4-t-BP were carried out in a 300 mL photoreactor equipped with a 10W UV lamp (Figure 1). The reactor was cylindrical with an external diameter of 50.8 mm and a length of 90 mm. Inlet flow rates ranged from 2.5 to 30 mL/min with the help of a peristaltic pump (Ismatec REGLO pump; IDEX Corporation, Lake Forrest, IL, USA). Ambient conditions of temperature and pressure were used, and approximately neutral pH conditions (6.7–7.1). Then, 15 mL aliquots of the treated solution were taken at different space times (10; 20; 40; 60 and 120 min) and filtered by means of 0.22 µm nylon filters. Each experiment was carried out in duplicates.

![Figure 1](image_url). Experimental setup for the continuous flow photodegradation of 4-t-BP.

2.3. Analytical Methods

The concentration of 4-t-BP was determined using an Agilent 1290 Infinity II high performance liquid chromatography (HPLC) unit equipped with a UV detector. The SB-C8 analytical column (2.1 × 100 mm, 1.8 µm) was operated at 25 °C. In a typical run, a sample of 1 µL was injected and the detection wavelength of 4-t-BP was set at 283 nm. A mixture of 50% MeOH and 50% ultrapure water was used as the mobile phase to elute the analytes at a flow rate of 0.4 mL/min.

TOC removal was determined by measuring the TOC in liquid samples by means of Multi N/C 3100, Analytic Jena AG Corporation (Jena, Germany). The pH of solutions was monitored using a Multi 9310 IDS meter.

3. Results and Discussion

3.1. UV-Photolysis

In order to gain insights into the performance of various UV-activated processes in continuous flow mode, a series of experiments in the absence of any catalyst and oxidant was performed by varying the space time (10, 20, 40, 60 and 120 min). The degradation of 4-t-BP steadily increased from 51.3 to 89.3% with the increase in space time from 10 to 120 min (Figure 2A). On the other hand, TOC removal did not significantly increase with increasing the space time above 20 min and the values observed were considerably
lower than the corresponding values for 4-t-BP degradation (Figure 2B). The increase in space time promotes both the formation of more reactive species and the contact between produced reactive species and pollutants, which, in turn, leads to higher degradation efficiencies. However, the TOC removal is not promoted to the same extent, as UV-photolysis alone cannot completely mineralize organic carbon [41–43]. For example, Wu et al. [13] achieved 60% 4-t-BP degradation after 300 min of 254 nm UV irradiation and observed the generation of several by-products, including 4-tert-butylcatechol, 4-tert-Butylphenol and 1-tert-butyl-2-methoxy-4-methylbenzene as an impurity. The results indicated that major degradation products of 4-t-BP were 4-tert-butylcatechol and 4-tert-Butylphenol dimer. Such intermediates were also detected in the UV (254 nm)/H₂O₂ system and prolongation of the process time to 16 h resulted in only 29% of TOC removal, confirming the persistent nature of generated by-products to mineralization.

3.2. UV/H₂O₂

Subsequently, the UV/H₂O₂ process’ efficiency was examined by varying the initial concentration of hydrogen peroxide (88.3 mg/L, 176.6 mg/L and 264 mg/L) and space time values (10, 20, 40, 60 and 120 min). The results obtained are shown in Figure 3 and agree with previous studies [12,21]. The UV/H₂O₂ process proceeds via direct photolysis and the formation of ·OH radicals that decompose most organic compounds without discrimination. Specifically, 93.34% of 4-t-BP degradation was observed after 10 min. This is due to the formation of sufficient amounts of hydroxyl radicals via the decomposition of H₂O₂ [44,45].

\[
H₂O₂ + hv \rightarrow 2 \cdot OH \tag{1}
\]

\[
\cdot OH + 4-t-BP \rightarrow \text{degradation products} \tag{2}
\]

As depicted in Figure 3A, degradation efficiency was not considerably affected by H₂O₂ concentration and space time. The concentration of 176.6 mg/L of H₂O₂ seemed to be the most beneficial one in terms of 4-t-BP degradation. Excessive doses of H₂O₂ beyond a certain value may have an inhibitory effect [46,47] through the initiation of propagation reactions that form perhydroxyl radicals (HO₂·), which are much less reactive than hydroxyl ones [48]. The detailed mechanism [49,50] is as follows (Equations (3)–(6)):

\[
\cdot OH + H₂O₂ \rightarrow HO₂· + H₂O \tag{3}
\]

\[
HO₂· + H₂O₂ \rightarrow \cdot OH + H₂O + O₂ \tag{4}
\]

\[
HO₂· + HO₂⁻ \rightarrow \cdot OH + HO⁻ + O₂ \tag{5}
\]

\[
\cdot OH + HO₂· \rightarrow H₂O + O₂ \tag{6}
\]

Figure 2. 4-t-BP degradation (A) and TOC removal (B) as a function of space time in the UV-photolysis.
Similar observations were made through TOC removal measurements. As a result, the values of \([\text{H}_2\text{O}_2]_0 = 176.6\) mg/L and space time = 60 min were selected as the desired conditions for further experiments.

![Figure 3](image)

**Figure 3.** 4-t-BP degradation (A) and TOC removal (B) as a function of space time in the UV/H\(_2\)O\(_2\).

The maximum TOC removal corresponding to 48.8% was achieved by applying \([\text{H}_2\text{O}_2]_0 = 264.9\) mg/L and space time = 120 min. The increase in TOC removal in the UV/H\(_2\)O\(_2\) system in comparison to UV-photolysis could be associated with the generation of both aromatic (4-tert-butylcatechol, 4-tert-butylphenol and 1-tert-butyl-2-methoxy-4-methylbenzene and hydroquinone) and non-aromatic products ((E)-2-Nonen-1-ol, trans-2-Decenol and (E)-2-Dodecen-1-al), where the latter are the result of a benzene ring fracturing process [13].

### 3.3. UV/Fe\(^{3+}/\text{H}_2\text{O}_2\) and UV/Fe\(^{2+}/\text{H}_2\text{O}_2\)

The effect of the presence of Fe\(^{3+}\) and Fe\(^{2+}\) ions on 4-t-BP degradation was also evaluated. The initial concentration of iron ions used was 5 mg/L. The reaction between iron and H\(_2\)O\(_2\) under UV light promotes the formation of OH [51] to effectively oxidize pollutants through Equations (7)–(14):

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad (7) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot \text{HO}_2 + \cdot \text{H}^+ \quad (8) \\
\cdot \text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2 + \cdot \text{H}_2\text{O} \quad (9) \\
\text{Fe}^{2+} + \cdot \text{OH} & \rightarrow \text{Fe}^{3+} + \cdot \text{OH}^- \quad (10) \\
\text{Fe}^{3+} + \cdot \text{HO}_2 & \rightarrow \text{Fe}^{2+} + \cdot \text{O}_2 + \cdot \text{H}^+ \quad (11) \\
\cdot \text{OH} + \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad (12) \\
4\text{-t-BP} + \cdot \text{OH} & \rightarrow \text{Intermediates} \quad (13) \\
\text{Intermediates} + \cdot \text{OH} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (14)
\end{align*}
\]

Figure 4A shows a similar oxidation performance for Fe\(^{2+}/\text{UV/}\text{H}_2\text{O}_2\) towards 4-t-BP degradation as in UV/\text{H}_2\text{O}_2 after 60 min of irradiation. The efficiency of Fe\(^{3+}/\text{UV/}\text{H}_2\text{O}_2\) was slightly lower. In contrast, an enhanced TOC removal (Figure 4B) was observed for the Fe\(^{3+}/\text{UV/}\text{H}_2\text{O}_2\) process, indicating a favorable Fe\(^{3+}\) contribution to the catalytic decomposition of \text{H}_2\text{O}_2 [52]. This can be attributed to a synergistic effect between Fe\(^{3+}\), UV and \text{H}_2\text{O}_2. TOC removal efficiencies followed the following order: Fe\(^{3+}/\text{UV/}\text{H}_2\text{O}_2\) > Fe\(^{2+}/\text{UV/}\text{H}_2\text{O}_2\) > UV/\text{H}_2\text{O}_2.
Figure 4. 4-t-BP degradation (A) and TOC removal (B) in the Fe$^{2+}$/UV/H$_2$O$_2$ and Fe$^{3+}$/UV/H$_2$O$_2$ at optimal conditions (conditions: space time = 60 min, 5 mg/L of catalyst, [H$_2$O$_2$] = 176.6 mg/L).

3.4. UV/TiO$_2$ and UV/Fe-TiO$_2$

The photocatalytic behavior of undoped TiO$_2$ and Fe-doped TiO$_2$ was examined for 4-t-BP degradation (Figure 5). The photocatalytic activity of Fe-TiO$_2$ relies on the dopant concentration [53–59]. Fe-TiO$_2$ at a mass ratio of 4% was selected as based on previously reported results [60,61].

Figure 5. 4-t-BP degradation (A) and TOC removal (B) as a function of space time in the UV/TiO$_2$ and UV/Fe-TiO$_2$.

As shown in Figure 5, 4-t-BP and TOC removals were apparently increased with an increasing space time from 10 min to 60 min for both TiO$_2$ and Fe-TiO$_2$, indicating substantial impact of space time on the performance of the systems. However, increasing space time from 60 min to 120 min resulted in apparently lower 4-t-BP degradation and TOC removal. Compared to pure TiO$_2$, the incorporation of iron particles slightly induced the degradation of 4-t-BP, degrading 87% after 60 min instead of 82%. This can be attributed to the retardation of the electron-hole pairs recombination [62]. It is noteworthy to mention that at lower space time (10 and 20 min), the performance of TiO$_2$ exceeded Fe-TiO$_2$, reaching 44.48% and 67% of 4-t-BP degradation in comparison to 33.41% and 55.79%, respectively. Comparatively, further increases in space time to 40 min and 60 min resulted in surpassed catalytic activity of Fe-TiO$_2$ over TiO$_2$.

3.5. Comparison of UV-Induced Processes

In order to compare the performance of UV-based processes, 4-t-BP degradation and TOC removal were plotted at the space time of 60 min. As observed in Figure 6A, the highest 4-t-BP degradation was achieved in the presence of H$_2$O$_2$ with the values ranging...
from 99.45% to 100% and followed the order of UV/H₂O₂ (264.9 mg/L) ≈ UV/Fe²⁺/H₂O₂ > UV/Fe³⁺/H₂O₂ > UV/H₂O₂ (176.6 mg/L) > UV/H₂O₂ (88.3 mg/L) > UV/Fe-TiO₂ > UV/Fe³⁺/H₂O₂ > UV only. Since the addition of H₂O₂ yield in a formation of higher amounts of hydroxyl radicals, the observed enhancement was expected. On the other hand, H₂O₂ concentration increase in UV/H₂O₂ system had an almost negligible effect on the degradation. As for the heterogeneous AOPs, the removal efficiency of 4-t-BP was 81.8% and 86.5% with TiO₂ and Fe-TiO₂ in the concentration of 200 mg/L, which indicates slight increased degradation of 4-t-BP than that of UV treatment only. It is worth mentioning that combination of continuous flow and UV/Fe-TiO₂ process contributed to the improvement of photo-oxidation reaction, while in a similar study [21] under batch-operated mode, the removal of 4-t-BP was higher by means of commercial TiO₂ than that of Fe-TiO₂.

Although 4-t-BP was largely degraded by almost all applied H₂O₂ concentrations after 60 min, the TOC removal varied from 20.05 to 41.66%. UV treatment alone did not provide significant levels of TOC removal, while removals around 50% were achieved within 60 min in the presence of heterogeneous photocatalysts (Fe-TiO₂ or TiO₂). Despite the low amount of Fe³⁺ added, its combination with H₂O₂ and UV led to the highest TOC removal (65%). The rank of TOC removal efficiency followed the order of UV/Fe³⁺/H₂O₂ > UV/TiO₂ > UV/Fe-TiO₂ > UV/Fe²⁺/H₂O₂ > UV/H₂O₂ (176.6 mg/L) > UV/H₂O₂ (264.9 mg/L) > UV only > UV/H₂O₂ (88.3 mg/L).

4. Conclusions

In the present work, various continuous-flow UV-mediated AOPs were used for the degradation of 4-t-BP and TOC removal in water. The results showed that 93.34% 4-t-BP degradation could be achieved at relatively low space time of 10 min in the UV/H₂O₂ system with oxidant concentration of 88.3 mg/L. The presence of H₂O₂ contributes to the highest degradation efficiencies, making homogeneous AOPs (UV/H₂O₂, UV/Fe²⁺/H₂O₂ and UV/Fe³⁺/H₂O₂) attractive for the removal of 4-t-BP.

Generally, flow rate had a positive effect on degradation efficiency, where optimal time to achieve the highest removal for most of the studied processes was found to be 60 min. As a result, the degradation performance improvement of UV, UV/TiO₂ and UV/Fe-TiO₂ was observed with the increase in space time. Moreover, the photocatalytic activity for TOC removal ability was also evaluated. Higher TOC removal efficiencies were observed in the catalyst-assisted systems. Approximately 65% of TOC abatement in less
than 60 min was achieved under UV/Fe\(^{3+}\)/H\(_2\)O\(_2\) treatment at an optimized concentration of H\(_2\)O\(_2\) (176.6 mg/L), probably because of the achieved synergistic effect between oxidant, catalyst, UV exposure and flow system. Overall, the findings propose attractive applications of continuous flow treatment systems for efficient water remediation contaminated with 4-t-BP.

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