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Electrochemical degradation of tebuthiuron pesticide using a flow reactor: Insights into the co-generation of oxidants and ecotoxicological risks

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ABSTRACT

Innovative contaminants treatment approaches are essential to addressing persistent environmental contamination from pesticides such as tebuthiuron (TBT), as they provide us with more effective and safer alternatives to traditional degradation methods. A notable advanced treatment approach is the combined electrochemical process which involves ultraviolet-C (UVC) activation of *in-situ* electrogenerated H_2O_2 and chlorine species – the combined UVC/e-H_2O_2@e-ClO^- system. This method uses an electrochemical flow reactor equipped with a gas diffusion cathode and a DSA®-Cl_2 anode, allowing the simultaneous production of both oxidants. Under the best experimental conditions (10 mA cm^{-2}, 10 mmol L^{-1} of Cl^-, and pH 7), the combined UVC/e-H_2O_2@e-ClO^- system promoted over 99.0% TBT degradation in 60 min of treatment and 63.2% total organic carbon removal in 90 min, with low energy consumption (1.54 kWh g^{-1} TOC). The roles of different reactive oxygen species (H_2O_2, HClO/ClO^-, and hydroxyl radicals ($HO^{\bullet}$)) were also evaluated, and a mineralization pathway was proposed based on the analysis of the by-products generated under the different electrochemical conditions. Although several by-products were detected during the degradation process, toxicological estimations suggested that these intermediates are less toxic than the parent compound; in this sense, it is evident that the degradation process helps reduce the environmental impact of TBT. Thus, the combined electrochemical process of activating H_2O_2 and chlorine species effectively degrades organic pollutants in chloride-containing wastewater, offering a sustainable and efficient treatment solution. Additionally, while TBT degradation has been extensively studied in the literature, it is the first time that a combined UVC/e-H_2O_2@e-ClO^- approach has been employed to investigate this contaminant and its toxicity effects following treatment.

***Keywords*:** electrochemical flow reactor, gas diffusion cathode, in-situ hydrogen peroxide, reactive chlorine species, tebuthiuron degradation, toxicological assessment.

1 Introduction

Electrochemical advanced oxidation processes (EAOP) are considered a highly promising technique for water treatment due to their adaptability and on-demand operationality. Unlike traditional methods, EAOPs can be used to treat matrices with varying contaminant levels; for instance, the treatment of industrial wastewater (effluent) often requires more treatment steps due to its higher contaminant concentration levels compared to raw water intended for human consumption. In view of that, EAOPs have been found to be extremely more efficient when applied for the treatment of industrial wastewater with high contaminant concentration levels and fluctuating water quality compared to raw water [1]. Furthermore, the decentralized nature of the EAOP treatment mechanism enables its deployment in diverse settings, from urban centers to remote communities [2]. However, most studies involving the use of EAOPs have focused their attention on the application of small-scale laboratory cells for wastewater remediation [3]. The present work aims to bridge this gap by using an electrochemical flow reactor (EFR) with higher flow rates to treat contaminants of high concentration in large-scale applications.

To add to the advantages of the EAOP technology, some studies have combined the process involving the electrogeneration of oxidants at the anode or cathode with UV irradiation or Fenton reaction to generate more reactive species [4]; however, these studies have typically been confined to a single electrode for either direct degradation or oxidant generation. To enhance the efficiency of EAOP systems, some studies have explored the co-electrogeneration of oxidants simultaneously at the anode and cathode, and often in combination with UV irradiation or Fenton reaction; one major shortcoming of these studies lies in their use of separate compartments with ion exchange membranes (IEM) to isolate and analyze the effects of each electrode process

[5–7]. As noted previously, the interaction of different oxidants within the same chamber can undermine the degradation efficiency [8,9]. Unfortunately, using IEM increases the costs of the electrochemical treatment system, and makes its maintenance quite difficult. To address these challenges, we propose the use of a membrane-less electrochemical system for the in-situ co-generation of oxidants for wastewater remediation purposes. To the best of our knowledge, no work reported in the literature has employed this approach to date.

The formation of toxic by-products in water treatment processes is a matter of huge concern, especially when the processes involve chlorine-based oxidants [10]. While these chlorine-based processes remove contaminants, they can also generate toxic by-products [11]. As pointed out in the literature, while chlorination can increase the toxicity of the treated solution, combining this treatment mechanism with UV light can help reduce the toxicity level [12,13]. Treatment systems that combine H_2O_2 with UVC often yield fewer toxic by-products. Oddly enough, there is an alarming scarcity of studies that have investigated the toxicity nature of the by-products formed during TBT degradation based on the combined application of electrogenerated H_2O_2 and hypochlorite (ClO^-) with UVC.

Tebuthiuron (TBT) is a widely popular herbicide which is commonly used for weed control mainly in sugar cane cultivations in Brazil; the compound is known for its very high persistence in the environment [14]. Because of its extremely high solubility in water (2.3 g L^{-1} at 25 °C), this pesticide is frequently detected in both surface water and groundwater [14]. TBT is regarded as highly toxic by the Brazilian Health Surveillance Agency in Brazil (ANVISA) [15]. Due to its characteristics, TBT was selected as model pollutant for the conduct of degradation analysis in the present study. A number of studies reported in the literature have investigated TBT degradation using

155 a wide range of alternative treatment technologies including electrochemical oxidation
156 with dimensional stable anodes [16], boron doped diamond anodes [17], UVC-based
157 technologies [18], and solar photo-Fenton [19]. In particular, the use of chlorine as
158 precursor of reactive oxygen and chlorine radicals in the aforementioned TBT
159 degradation techniques has been found to present some underlying disadvantages; these
160 include the possible formation of organochlorine compounds and concerns regarding
161 environmental safety with respect to the use of chlorine. Among the main advantages of
162 the in-situ co-generation of oxidants such as H_2O_2 and ClO^- and its activation using
163 UVC include the following: i) lack of the need for oxidants transportation, and ii) highly
164 efficient and fast contaminants degradation rates. It is worth highlighting that the central
165 idea of our proposed treatment approach lies in using a Printex® L6 carbon gas diffusion
166 electrode, which is well known for its high selectivity for H_2O_2 generation, and a
167 commercial DSA® anode, which is widely recognized for its ability to generate chlorine
168 species. In essence, by employing these electrodes in the treatment system, the approach
169 is expected to promote high degradation efficiency from the successful combination of
170 the electrogenerated oxidants. The identification of by-products formed during TBT
171 degradation and the analysis of their toxicity are found to be of great importance.
172 Indeed, among the main novel contributions of the present study is the use of suitable
173 tools to estimate acute and chronic toxicity in TBT degradation for the first time under
174 the proposed treatment system.

175 In short, the present study employs for the first time an electrochemical flow
176 reactor in a recirculation system for the *in-situ* electrogeneration of H_2O_2 and ClO^-
177 oxidants targeted at the degradation of TBT herbicide. Different treatment systems -
178 including photolysis (UVC), anodic oxidation (AO), electrogenerated H_2O_2 and ClO^-
179 oxidants (e-H_2O_2 and e-ClO^-), and their combinations were evaluated. The study also

investigated the role of the electrogenerated oxidants and radical species ($ClO^{\bullet}$, $Cl^{\bullet}$ and $HO^{\bullet}$) in TBT mineralization, and pathways for TBT degradation were proposed. In addition, we also conducted a toxicological analysis of the by-products formed using a Quantitative Structure-Activity Relationship (QSAR) model.

2 Materials and Methods

2.1 Chemicals

The following compounds were used for the preparation of the electrolyte and for pH control: potassium sulfate (K_2SO_4), sodium chloride (NaCl), sulfuric acid (H_2SO_4), and potassium hydroxide (KOH) - all chemicals were of 99.9% purity. H_2O_2 was quantified using the complexing 0.5 mol L^{-1} H_2SO_4 solution containing ammonium molybdate ($(NH_4)_6Mo_7O_{24}$). For the preparation of the electrode, we employed a commercial Printex L6 carbon (PL6C) (purchased from Evonik) mixture with poly(tetrafluoroethylene) (PTFE, 60% aqueous dispersion) - obtained from Daklon 1 (Sealflon). For the construction of the calibration curves using the analytical procedure, we employed standard tebuthiuron (purchased from Sigma-Aldrich). For the degradation process, we prepared a solution concentration of 100 μmol L^{-1} of the pesticide tebuthiuron with 50% *w*/*V* (commercial grade) - acquired from Dow AgroScience (Combine 500 SC). All solutions were prepared using ultrapure water, obtained from the Milli-Q system (resistivity >18 MΩ cm).

2.2 Preparation of Gas Diffusion Electrode (GDE)

The gas diffusion electrode (GDE) was prepared based on the method previously described by our research group [20]. Briefly, the gas diffusion layer was prepared by

mixing PL6C with PTFE. The mixture containing PL6C and PTFE was prepared in the ratio of 80 (PL6C) to 20 (PTFE) (*w*/*w*). The mixture was spread on a thin layer over carbon cloth - obtained from ZOLTEK. Finally, the mixture/cloth was hot pressed by applying 4.5 tons at 290 °C for 15 min.

2.3 Electrochemical Flow Reactor Setup

The electrochemical flow reactor (EFR) used in this work has already been characterized and reported in a previous work published in the literature [21]; the EFR design is presented in Fig. 1. The GDE, used as cathode, is sequentially connected to a stainless-steel mesh (current collector) and a gas chamber filled with O_2. A dimensionally stable anode with chlorine (DSA®-Cl_2) (from De Nora do Brasil) was used as anode. Both electrodes (GDE cathode and DSA®-Cl_2 anode) had an exposed geometric area of 20 cm^2.

Fig. 1. **a)** EFR configuration; **b)** internal design of the flow reactor with gap between the electrodes.

The system setup used for TBT degradation is presented in Fig. 2. A semi-batch configuration was used; the system consisted of a reservoir tank (with 1.0 L solution), where the temperature (~22.0 °C) is controlled using a thermostatic bath. A power source controlling the current passing through the EFR is fed by a peristaltic pump operating at the flow rate of 30 L h^{-1}. Behind the outlet of the EFR, a chamber containing a low-pressure Hg lamp (254 nm; Philips 9W) is used to activate the electrogenerated oxidants. The gas flow rate is controlled by a flow meter and fed by an O_2 (99.9% purity) cylinder.

Fig. 2. Electrochemical Setup: **1)** Electrochemical flow reactor; **2)** UVC chamber; **3)** Reservoir tank; **4)** Peristaltic pump; **5)** Power source; **6)** Gas flow meter; **7)** Oxygen cylinder.

The electrogenerated H_2O_2 was quantified by an indirect method using a complexant of ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) solution at 2.4×10^{-3} mol L^{-1} [10]. The complex formed (peroxymolybdate) was very stable, with absorbance measured at the wavelength of 350 nm. The analysis was performed using a UV-1900 spectrophotometer (Shimadzu) and a quartz cuvette with 1 cm path length.

The power source was connected to two multi-meters (one in parallel and the other one in series) in order to guarantee the accuracy of the current and potential (measured). As reported, the EFR employed in this work has been previously studied and its current range efficiency has already been determined [21]. Taking these observations into account, the applied current range that would ensure the presence of enough H_2O_2 for TBT degradation was set at 0.1 to 0.3 A (or 5 – 15 mA cm^{-2}). Although the conductivity of wastewater is observed at 15 mS cm^2, we employed the ionic strength of 0.3 mol L^{-1} as control. In the tests involving the use of NaCl as a source of Cl^- ions, conductivity was adjusted, maintaining the same ionic strength.

2.4 Analytical Procedures

The degradation of TBT, salicylic acid (Sac. Ac.), 2,3 and 2,5 dihydroxybenzoic acid (2,3 and 2,5 DHBA) was analyzed by high-performance liquid chromatography (HPLC) using Shimadzu 20A LC system with a UV detector. A reversed-phase C18 column was used as the stationary phase (150 mm × 4.6 mm, 5 µm particle size, from

249 Phenomenex). All the analytical methods were first validated by calibration curves
250 constructed using standard TBT; this was done in order to determine the concentration
251 range, limit of detection (LOD), limit of quantification (LOQ), and linearity. All the
252 samples collected were filtered using a 0.45 µm Chromafil®Xtra PET filter (Macherey-
253 Nagel) before analysis, and recovery tests were conducted with and without sample
254 filtration.

255 For the analysis of only TBT degradation, we used a mobile phase which
256 consisted of a mixture of 70% acetonitrile and 30% ultrapure water at a flow rate of 1
257 mL min^{-1}; elution was done in the isocratic mode. The standard range for the calibration
258 curve was 0.31 - 20 mg L^{-1}, with linearity of R^2=0.9993 as the correlation. The limit of
259 detection (LOD) and limit of quantification (LOQ) were 1.56 x 10^{-2} mg L^{-1} and 4.7 x
260 10^{-2} mg L^{-1}. The recovery percentage obtained was 99.9%, with and without filtration.
261 For Sac. Ac., 2,3 and 2,5 DHBA, a gradient elution method with a mixture of 50%
262 acetonitrile and 50% aqueous solution of formic acid (0.1%) was employed. The sample
263 injection employed was 20 µL and the wavelength monitoring for TBT, Sac. Ac., 2,3
264 and 2,5 DHBA was performed at 254, 300, 315 and 335 nm, respectively. The standard
265 concentration range for the calibration curve was 3.1 - 125 mg L^{-1} for the three
266 compounds, with linearity of R^2=0.995 as the correlation. The LOD recorded for Sac.
267 Ac., 2,3 and 2,5 DHBA was 3.4x10^{-2}, 1.0x10^{-2} and 1.7x10^{-2} mg L^{-1}, respectively, while
268 the LOQ recorded for Sac. Ac., 2,3 and 2,5 DHBA was 0.1, 5.3x10^{-2} and 3.3 mgL^{-1},
269 respectively. For all the three compounds investigated, the recovery percentage obtained
270 was 98.5%, with and without filtration.

271 The anions (NO_3^-) were monitored by ion chromatography using Metrohm 850
272 PRO IC coupled to Vario 940IC Extension Module with a conductivity detector. The
273 MetrosepA Supp 5 column (150 mm/4.0 mm) was used as stationary phase for the

anionic species at 25 °C. The mobile phase, which was employed at a flow rate of 0.7 mL min^{-1}, consisted of Na_2CO_3 and $NaHCO_3$ (3.2 and 1.0 mmol L^{-1}, respectively). The standard concentration range for the calibration curve was 0.5 - 16 mg L^{-1}, with linearity of R^2=0.991 as the correlation. The LOD and LOQ recorded were 0.3 mg L^{-1} and 1.1 mg L^{-1}, respectively. The recovery percentage obtained was 92%, with and without filtration. The rate of mineralization was evaluated through the analysis of total organic carbon (TOC) using Shimadzu TOC-VCPN. The standard concentration range for the calibration curve was 1.0 - 50 mg L^{-1}, with linearity of R^2=0.991 as the correlation.

The intermediates formed during the TBT degradation process were also determined by liquid chromatography tandem mass spectrometry (LC–MS/MS). However, for the separation and detection of by-products, the elution was performed in gradient mode as described as follows: the LC-MS/MS analysis was performed using LC 20AD XR Shimadzu chromatograph with Shim Pack C-18 reversed-phase as stationary phase (100 mm × 3.0 mm, 2,2 μm particle size, from Shimadzu®) and a mixture of H_2O (A) and acetonitrile (B), both acidified with 0.1% formic acid, as mobile phase. The gradient elution, employed at a flow rate of 0.8 mL min^{-1}, was carried out in the following conditions: 0-5 min: 10-37% B; 5-8 min: 37-100% B; 8-10 min: 100-10% B. The injection volume and column temperature employed were 10 μL and 26 °C, respectively. The chromatographic system was coupled to 8030-quadrupole mass spectrometer (Shimadzu, Kyoto, Japan), which operated under an electrospray interface, in positive mode. The MS/MS conditions applied were as follows: curtain gas at 20 psi, ion spray at 4000 V, desolvation temperature of 250 °C, and ion source temperature of 400 °C. Selected ion monitoring (SIM) and full scan experiments were performed automatically.

The calculated value of specific electrical consumption per unit TOC mass (EC_{TOC}) was defined by kWh g^{-1} TOC. This value can be derived from Eq. 1, where E_{cell} is the cell potential (in V), I is the applied current (in A), V is the wastewater volume (in L), and ΔTOC_{exp} is the TOC removed (in mg L^{-1}) at time t (in h); for the experiment involving the use of UVC lamp, Eq. 1 is also used considering the electrical energy associated with the use of lamp, where P is the nominal power (in W):

$$E_{TOC}(\text{kWh } g^{-1}\text{TOC}) = \frac{E_{cell} I x t + P\ t}{V(\Delta TOC)_{exp}} \qquad \textbf{Eq. 1}$$

2.5 Ecotoxicological Assessment

The ecotoxicological effects (LC_{50}) of some chlorinated degradation by-products of TBT in fish (*Fathead minnow, 96 h)* and crustaceans (*Daphnia magna,* 48h) were predicted/estimated using the Computational Toxicology and Exposure Online Resources (Comptox) tool. This safe chemical analysis program relies on Quantitative Structure-Activity Relationship (QSAR) models to estimate toxicity based on the physical characteristics of the structures and the experimental data obtained from many reliable sites, databases, sources, including the U.S. Federal and State sources, and international agencies. For this study, the Toxicity Estimation Software Tool (T.E.S.T) version 5.1 was used for the analysis of toxicity, since it possesses the highest number of tests available in the literature with good prediction results [22].

3 Results and Discussion

3.1 Optimization of Parameters for TBT Degradation

In this section, we evaluated the effect of key operating conditions, such as current density, added Cl^- concentration and pH, on the degradation of TBT solution (100 µmol L^{-1}) using an EFR operated under the combined system which involved the

simultaneous electro-generation of H_2O_2 and ClO^- in the presence of UVC light. The optimization of these parameters is fundamentally important because it leads to significant improvements in TBT degradation efficiency, in addition to minimizing energy consumption and maximizing the resulting environmental benefits. Operating under optimized parameters not only improves the performance of the degradation process, but also provides us with ample metrics for comparing the results of this study with those reported in the existing literature.

Under the UVC/e-H_2O_2@e-ClO^- process, the electrochemical production of H_2O_2 and reactive chlorine species is expected to occur through the action mechanism of suitable cathodes and anodes. At the cathode, H_2O_2 is produced through oxygen reduction reaction via a two-electron mechanism (2e-ORR) (**Eq. 2**)[23]; on the surface of the DSA®-Cl_2 anode, active chlorine (in the form of Cl_2) is generated through Cl^- anodic oxidation via **Eq. 3**. Cl_2 diffusion in the bulk solution can occur disproportionately to hypochlorous acid (HClO) and Cl^-, as shown in **Eq. 4**. In solution, HClO is in equilibrium with hypochlorite ion (ClO^-), as can be noted in **Eq. 5** [24].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 (E^0 = 0.68 \text{ V Vs NHE}) \qquad \textbf{Eq. 1}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- (E^0 = 1.36 \text{ V Vs NHE}) \qquad \textbf{Eq. 3}$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \qquad \textbf{Eq. 4}$$

$$HClO \rightleftharpoons ClO^- + H^+ \quad pKa = 7.5 \qquad \textbf{Eq. 5}$$

It has been well documented that under UVC irradiation, H_2O_2 and ClO^- can promote the formation of other stronger reactive agents. For instance, the activation of H_2O_2 by UVC leads to the production of hydroxyl radical ($HO^\bullet$) (**Eq. 6**) (Zhao et al.,

2022), while chlorine radical ($Cl^{\bullet}$) and $HO^{\bullet}$ are generated from the homolysis of HClO and ClO^{-}, as demonstrated in **Eq. 7** [25].

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \qquad \textbf{Eq. 6}$$

$$HClO/ClO^{-} + h\nu \rightarrow Cl^{\bullet} + HO^{\bullet}/O^{\bullet -} \qquad \textbf{Eq. 7}$$

According to the literature, by increasing the current density (*j*), one enhances the production of active chlorine on the surface of the DSA®-Cl_2 anode [4] and H_2O_2 on GDEs made of PL6C [10,26]. However, a progressive increase of *j* during H_2O_2 electrogeneration leads to parallel reactions, which are favored at higher overvoltage (overpotential)[5]. Taking these observations into account, the present study evaluated the effects of applying different current densities; the current densities evaluated were in the range of 5 -15 mA cm^{-2}, as shown in Fig. 3a.

It is worth pointing out that, since the GDE cathode was made of porous carbon material, a control experiment was performed, without the application of current, in order to ensure that there was no adsorption of TBT on the electrode; the result of this experiment showed that there was no decrease in TBT concentration in the system after 90 min of electrolysis.

Fig 3. a) TBT degradation based on the application of UVC/e-H_2O_2@e-ClO^{-} at different current densities; **b)** effect of NaCl concentration on TBT degradation; and **c)** effect of pH on TBT degradation. **Inset:** % of TOC removed from initial solution.

The analysis of TBT degradation (Fig. 3a) points to a two-step process. As shown in Fig. S-1, the first 15 min stage exhibits slow kinetics, while the second stage

shows a faster kinetic rate that varies depending on the applied conditions. These outcomes are likely linked to the accumulation of oxidants within the system before their activation and will be thoroughly discussed in section 3.3. A first-order kinetic model fits well for all the curves. The rate constant (k, min^{-1}) presented in Table 1 is associated with the second step and was obtained from the slope of **Eq. 8**, where C_0 and C are the initial and final concentrations (mg L^{-1}) of TBT, respectively, at time t.

$$\ln \frac{C_0}{C} = k\, t \qquad \textbf{Eq. 8}$$

Table 1. Effects of different parameters on TBT degradation and the amount of electrical energy consumed in the degradation process.

UVC/e-H_2O_2@e-ClO^-				
Parameter	**TBT removal t_{60min} (%)**	***k* (min^{-1})**	**R^2**	**TOC Removal t_{90min} (%)**
***j* (mA/cm^2)[a]**				
15	99.1	$8.556\ 10^{-2}$	0.97	71.2
10	99.4	$8.573\ 10^{-2}$	0.93	62.1
5	95.6	$5.087\ 10^{-2}$	0.91	39.0
NaCl (mM)[b]				
15	99.4	$8.573\ 10^{-2}$	0.93	62.1
10	99.5	$8.820\ 10^{-2}$	0.95	63.2
5	99.4	$8.143\ 10^{-2}$	0.91	59.6
pH[c]				
3	98.2	$6.361\ 10^{-2}$	0.91	48.2
7	99.5	$8.820\ 10^{-2}$	0.95	63.2

Electrolysis condition
[a] [K_2SO_4] =45 mM; [Cl^-]= 15 mM; pH = 7.0
[b] current density =10 mA cm^{-2}; pH =7.0
[c] current density = 10 mA cm^{-2}; Cl^- =10 mM

The plot in Figure S-1 shows a slow degradation rate in the first 15 min of treatment; oxidation occurs faster after this period. This behavior can be observed in all

the operating conditions. To understand the reasons behind this variation, it is important to consider that at the initial stages of the degradation process, the concentration of oxidants is still increasing. This observation has been made in a previous study conducted using a PL6C-based GDE in similar conditions [10]. A similar effect is expected regarding the kinetics involving the generation of active chlorine in DSA®-Cl_2-type anodes [27].

Likewise, increasing *j* also leads to an increase in TOC removal (inset in Fig. 3a and Table 1). At low current density (5 mA cm^{-2}), there is a mild organic compound remediation (up to 39% of TOC removal), while a greater rate of mineralization is observed at 10 mA cm^{-2} (62.1%) and 15 mA cm^{-2} (71.2 %) – all after 90 min of treatment. Furthermore, the NO_3^- being monitored, which is a by-product of TBT degradation, is also favored at the current densities ranging from 10 to 15 mA cm^{-2} (see Fig. S-3a); this shows that higher current densities are more suitable for TBT mineralization. It should be noted, however, that the presence of NO_3^- may lead to an increase in the genotoxicity of the treated solution, apart from inhibiting H_2O_2 formation, as reported in other works [28]. Thus, 10 mA cm^{-2} was found to be the most suitable current density, since raising the current density above this limit leads to more energy consumption and an unwanted increase in NO_3^- concentration.

The effect of added Cl^- concentration (5-15 mmol L^{-1}) - another key parameter that is expected to influence the concentration of oxidants generated and the efficiency of the degradation process, was evaluated at the current density of 10 mA cm^{-2} and pH of 7.0 (Fig 3b). In this study, the variation of Cl^- is reflected in the concentration range observed in real water matrices ranging from 200 to 500 mg L^{-1}, which is equivalent to between 5.6 and 14 mmol L^{-1} [29]. An increase in Cl^- concentration slightly affects the

removal of TBT or TOC. This behavior can be linked to the fact that the excessive concentration of HClO/ClO^- can scavenge the $HO^\bullet$ and $Cl^\bullet$ generated, as can be seen in **Eqs. 10-13** [30], and HClO can react with H_2O_2, as shown in **Eq. 9**. Moreover, this effect can be easily observed in Fig. S-2, which presents a comparative analysis of the electrogeneration of H_2O_2 in different conditions, in the presence and absence of TBT and other scavengers (e.g. UVC, HClO/ClO^-).

$$H_2O_2 + HOCl \rightarrow O_2 + H_2O + H^+ + C1^- \quad \textbf{Eq. 9}$$

$$HO^\bullet + OHCl \rightarrow ClO^\bullet + H_2O \quad \textbf{Eq. 10}$$

$$HO^\bullet + OCl^- \rightarrow ClO^\bullet + OH^- \quad \textbf{Eq. 11}$$

$$Cl^\bullet + HOCl^- \rightarrow ClO^\bullet + H^+ + Cl^- \quad \textbf{Eq. 12}$$

$$Cl^\bullet + OCl^- \rightarrow ClO^\bullet + Cl^- \quad \textbf{Eq. 13}$$

Regarding the formation of NO_3^-, the addition of Cl^- led to a decrease in the concentration of NO_3^- detected; this shows that the presence of chlorine affects the formation of NO_3^- species (Fig S-3b), probably due to the chlorination of TBT, instead of its mineralization, as we will see further in this work. Also, an increase in NO_3^- formation led to a decrease in H_2O_2 accumulation. After 90 min of treatment, the experiments involving the use of an initial concentration of 5, 10 and 15 mM of Cl^- generated 2.1, 2.9 and 3.9 mg L^{-1} of NO_3^-, respectively, while the corresponding H_2O_2 concentrations produced were 122.9, 98.1 and 75.8 mg L^{-1}. In the presence of 10 mmol L^{-1} of Cl^-, we observed slight improvements in both TBT degradation and NO_3^- formation. Based on these results, the current density of 10 mA cm^{-2} and the Cl^-

concentration of 10 mmol L^{-1} were chosen (constant) for the conduct of subsequent experiments for the analysis of the effect of pH variation.

The effect of initial pH (3.0 and 7.0) on TBT degradation was also evaluated. Fig. 3c shows that by changing the pH from 3.0 to 7.0, TBT removal is slightly affected; however, in terms of TOC removal, it is clear that pH 7.0 outperforms pH 3.0. It is known that in the pH range of 3-7, the predominant active chlorine species is HClO, and an increase in pH leads to a corresponding increase in ClO^- ions [31].

Looking into the existing literature, one will observe that very few studies have employed co-generated oxidants in electrochemical systems for water remediation purposes. Table 2 (indexes 1-3) presents an outline of some studies reported in the literature where both cathode and anode have been used for the simultaneous production of oxidant species, in conjunction with UV light, aimed at water remediation. These studies have commonly employed different cathodes to generate H_2O_2, while the anode has primarily produced chlorine species. The studies presented in indexes 1 and 2 employed low pollutant concentrations (0.1-5.0 mg L^{-1}), where they obtained rapid pollutant removal within minutes of treatment; it should be noted, however, that study 2 required approximately 60 minutes of electrolysis to obtain 57.8% mineralization. In study 3, an Sb-doped anode produced hydroxyl radicals ($HO^{\bullet}$) which helped promote the removal of high concentrations of phenol (94 mg L^{-1}); the study recorded a complete contaminant removal after 60 minutes of treatment, though only 40% mineralization was obtained.

While no studies reported in the literature have investigated TBT degradation using co-generated oxidants, some studies have employed electrochemical systems for TBT degradation for comparison purposes, as shown in Table 2 (indexes 4-6). These

studies employed different electrochemical advanced oxidation processes (EAOP) to degrade approximately 100 mg L^{-1} of TBT. In studies 4 and 5, H_2O_2 production occurred at the cathode, while boron-doped diamond (BDD) was used as the active anode. In study 6, a DSA® anode was used to generate Cl_2 (as the oxidant), while an inactive stainless steel was used as cathode. All the three studies mentioned above required about 120 minutes of electrolysis to eliminate 100 mg L^{-1} of TBT, but mineralization only occurred after 300 to 540 min of treatment.

For comparison purposes, the method proposed in our present study (index 7), which involved the co-generation of oxidants with UV irradiation, promoted 100% TBT degradation in 60 min of treatment and a remarkable 63.2% mineralization rate in one-third of the time reported by the other methods. These results show that the application of the proposed mechanism, which involved the co-generation of oxidants in the presence of UV irradiation, significantly enhances the efficiency of electrochemical systems used in environmental remediation.

For a comparison of energy consumption during the degradation process, a comparative analysis of specific electrical consumption per unit TOC mass was performed with a view to comparing the amount of energy consumed in the proposed system with that of the other studies conducted on TBT degradation. As it is evident, the proposed system required relatively lower amount of energy for TOC removal compared to the other studies. It is worth noting that with the application of low pressure Hg lamps (9W UVC in the present study), the amount of energy consumed in the proposed system was quite low compared to that of other systems in which UVA or UVC was employed – where high-pressure Hg lamps were mainly applied. In essence, this is one of the key advantages of the proposed system. Furthermore, the use of highly

efficient anodes for the cathodic and anodic formation of oxidants also helps to explain the high efficiency of this system compared to other similar systems.

Table 2. Comparative analysis of different EAOPs applied for contaminants degradation in previous studies reported in the literature.

Index	Cathode (oxidant)	Anode (oxidant)	UV irradiation	Contaminant	Degradation	TOC removal	Energy consumption	Ref.
1	C-PTFE (H_2O_2)	DSA® (Cl_2)	UV	Ibuprofen, gemfibrozil, naproxen, and diclofenac	84-100 % (after 5.6 min)	-	-	[7]
2	modified graphite felt (H_2O_2)	DSA® (Cl_2)	UV	carbamazepine	100 % (after 4 min)	57.8 % (after 60 min)	1.12 kWh/m^3 $order^{-1}$	[32]
3	carbon nanotube (H_2O_2)	Sb-doped ($HO^{\bullet}$)	-	Phenol	100 % (after 60 min)	40 % (after 60 min)	0.12 kWh g-TOC^{-1}	[6]
4	carbon-PTFE air-diffusion (H_2O_2)	BDD	UVA	Tebuthiuron	100 % (after 180 min)	>90 % (after 540 min)	-	[33]
5	GDE (H_2O_2)	BDD	UVC	Tebuthiuron	87.9 % (after 120 min)	~95 % (after 360 min)	~ 45 kWh m^{-3} $order^{-1}$	[26]
6	stainless steel	DSA® (Cl_2)	UVC	Tebuthiuron	100 % (after 120 min)	100 % (after 300 min)	3.0 kW h g^{-1} TOC	[24]
7	GDE (H_2O_2)	DSA® (Cl_2)	UVC	Tebuthiuron	100 % (after 60 min)	63.2 % (after 90 min)	1.5 kWh g^{-1} TOC	This work

3.2 Contributory Effect of Combined EAOPs Applied in TBT Degradation

The combined UVC/e-H_2O_2@e-ClO^- process exhibited a good performance when applied for TBT degradation under optimized experimental conditions (i.e., 10 mA cm^{-2}; 10 mmol L^{-1} of Cl^-; and pH 7); however, to better understand the contribution of each system in the degradation process, control experiments were performed using the following processes: photolysis (UVC), anodic oxidation (AO), e-H_2O_2, e-ClO^-, UVC/e-H_2O_2, UVC/e-ClO^-, and UVC/e-H_2O_2@e-ClO^-. Fig. 4 shows the results obtained from the comparative analysis of different EAOPs applied for TBT degradation; the results show the contribution of each process in the contaminant

475 removal and mineralization. In addition, the TOC results were used to calculate the
476 contribution of each process and the energy costs involved, as described in **Eq. 1**.

477

478 **Fig. 4**. **a)** TBT degradation curve; **b)** TOC removal after 90 min of treatment; **c)**
479 Contribution of each process in TOC removal; **d)** Electrical energy consumed per gram
480 of TOC removed, based on the application of different EAOPs investigated in this
481 study.

482 The TBT degradation curves obtained from the application of the different
483 treatment systems are presented in Fig. 4a. As can be noted, three processes exhibited
484 the most efficient results in terms of TBT degradation: i) UVC/e-H_2O_2; ii) UVC/e-ClO^-
485 – each electrogenerated oxidant in the presence of UVC; and iii) the combined UVC/e-
486 H_2O_2@e-ClO^- process. Among these three processes, the combined UVC/e-H_2O_2@e-
487 ClO^- system exhibited the best degradation rate, recording 99.0% TBT degradation in
488 60 min of treatment; this was followed by UVC/e-H_2O_2 and UVC/e-ClO^- with 97.3 and
489 89.7% degradation rates, respectively, for the same treatment time. Yin H. et al. (2021)
490 obtained similar results when they studied the use of activated electrogenerated chlorine
491 and H_2O_2 in the presence of UV for the degradation of different contaminants; in their
492 study, the combined UV/E-Cl&H_2O_2 system also exhibited the best performance in
493 terms of contaminants removal compared with UV/E-Cl and UV/E-H_2O_2. In the
494 aforementioned study conducted by Yin et al. (2021), the authors also found that the
495 combined UV/e-Cl&H_2O_2 system exhibited superior performance when they tested
496 different water matrices (including lake water, secondary wastewater effluent, and
497 medical wastewater); this clearly points to the versatility of the combined system, as it
498 can be employed for a wide range of purposes [32].

To better evaluate the ability of each EAOP to remove organic matter in the system, TOC analysis was used to estimate the rate of mineralization (see Fig. 4b). This approach allows one to have a better understanding of the process involving the decontamination of the by-products formed after the target compound has been eliminated. For this analysis, the electrolysis lasted 90 min. Once again, the UVC/e-H_2O_2@e-ClO^- system exhibited the best performance; it recorded 63.2% TOC removal in 90 min. An interesting result was observed in terms of TOC removal when the process containing only H_2O_2(AO-e-H_2O_2 and UVC/e-H_2O_2) was compared with that containing only chlorine (AO-e-ClO^- and UVC/e-ClO^-). After 90 min of electrolysis, the AO-e-H_2O_2 processes recorded 14.2% TBT degradation (Fig. 4-a), with 9.5% TOC removal (Fig. 4-b); however, with the addition of UVC, these values increased to 99.8% (TB degradation) and 51.2% (TOC removal), respectively. The AO-e-Cl^- process recorded a better TBT degradation rate (31.4%), but with low TOC removal (3.5%); interestingly, the combination of the system with UVC (UVC/e-Cl^-) resulted in 99.4% TBT degradation, with 26.3% TOC removal. These results show that chlorine species exert a more significant effect on TBT degradation (this is probably related to the chlorination of the molecule), whereas H_2O_2 exerts a more significant effect on TOC removal (which is probably related to high oxidation of $HO^{\bullet}$ radical).

To separate the contribution of the EAOP technology in TOC removal, we subtracted the contribution values derived from the AO and UVC (obtained from control experiments) from the values recorded for the combined processes: AO-e-H_2O_2, AO-e-ClO^-, UVC/e-H_2O_2, UVC/e-ClO^-, and UVC/e-H_2O_2@e-ClO^-. The results obtained are presented in Fig. 4c; as can be observed, UVC exerts a much higher contribution (17.3 %) in TOC removal compared to AO (2.9 %). As expected, UVC irradiation also exerts a significant effect on H_2O_2 and ClO^- by producing $HO^{\bullet}$ and

radical chlorine species (RCS)[24]. After subtracting the effect of UVC and AO from the other conditions, one can clearly see the synergistic effects. The value of TOC removal recorded for the UVC/e-H_2O_2 and UVC/e-ClO^- processes was 31.0% and 6.13%, respectively. For the combined process (UVC/e-H_2O_2@e-ClO^-), the rate of TOC removal derived from RCS and $HO^{\bullet}$ only was 39.8%, which is approximately the sum of the values recorded for the UVC/e-H_2O_2 and UVC/e-ClO^- processes. Thus, the combined UVC/e-H_2O_2@e-ClO^- system recorded an increase of 8.8% in TOC removal compared to UVC-e-H_2O_2 – the second highest.

Other works reported in the literature have shed light on the role of the combined treatment processes, and have pointed out their contribution to the treatment of a wide range of pollutants [32]. Zhang et al. (2022) obtained interesting results in their study on the use of ultraviolet irradiation with electrochemical chlorine and hydrogen peroxide production for the degradation of gemfibrozil, ibuprofen, and naproxen; in this study, the authors found that the combined application of UV and electrogenerated Cl_2 produced efficient results in terms of gemfibrozil and naproxen degradation, but the technique proved ineffective for the degradation of ibuprofen. By contrast, the e-UV/H_2O_2 process yielded effective results in terms of ibuprofen removal, yet was less effective for gemfibrozil and naproxen removal.

The amount of energy consumed (E_{TOC}) based on the contribution of each EAOP system is presented in Fig. 4d. The E_{TOC} value was calculated based on the analysis of TBT (100 μmol L^{-1}) and by-products degradation after 90 min of electrolysis, where 63.2% removal was recorded. The effect of TBT degradation observed in the experiment conducted using only UVC served as a reference for separating the amount of energy consumed by the electrochemical reactor. The UVC system exhibited higher levels of energy consumption, with UVC/e-H_2O_2, UVC/e-ClO^- and UVC/e-H_2O_2@e-

549 ClO^- recording 1.7, 3.5 and 1.5 kWh g^{-1} TOC, respectively. Gozzi et al. (2017)
550 employed a flow plant of 2.5 L, equipped with a boron-doped diamond (BDD)/air-
551 diffusion cell and a solar planar photoreactor, to degrade 0.18 mmol tebuthiuron using
552 anodic oxidation combined with the following different processes: electrogenerated
553 H_2O_2 (AO-H_2O_2), electro-Fenton (EF) and solar photoelectro-Fenton (SPEF); based on
554 the results of the study, the EF and SPEF processes yielded the best results – EF: energy
555 consumption of 1.0 kWh g^{-1} TOC, current density of 25 mA cm^{-2}, and 42% TOC
556 removal; SPEF: energy consumption of 0.41 kWh g^{-1} TOC, current density of 50 mA
557 cm^{-2}, and 41% TOC removal. In our present study, the high energy consumption
558 recorded for all the systems that involved the use of UVC can be attributed to the Hg
559 lamp (254 nm), which consumes 9 W h^{-1}, since the maximum amount of energy
560 consumed by the electrochemical reactor in the UVC/e-H_2O_2@e-ClO^- system was only
561 0.12 kWh g^{-1} TOC.

562 *3.3 Role of $HO^\bullet$ Species in TBT Degradation*

563 Based on the results presented in the previous sections, it is clear that the
564 UVC/e-H_2O_2 and UVC/e-H_2O_2@e-ClO^- processes exhibited high efficiency when
565 applied for TBT degradation. This observed effect can be directly attributed to the
566 generation of $HO^\bullet$ species from the photolysis of the electrogenerated H_2O_2 and ClO^-.
567 Thus, electrolysis tests were carried out using salicylic acid (Sac. Ac.), a well known
568 scavenger of $HO^\bullet$, in order to determine the role of $HO^\bullet$ species in each treatment
569 process [34–36]. It is worth mentioning that the rate constant related to the
570 hydroxylation reaction of Sac. Ac. in 2,5-DHBA is slightly higher than that of 2,3-
571 DHBA (2.4×10^{10} L mol^{-1} s^{-1} vs. 1.3×10^{10} L mol^{-1} s^{-1}) [34]. The decomposition of Sac.
572 Ac. and the formation of the intermediate dihydroxybenzoic acid (DHBA) are shown in
573 Fig. 5, for all the processes involving H_2O_2 (i.e., AO/e-H_2O_2, UVC/e-H_2O_2, and UVC/e-

574 H_2O_2@e-ClO^-). Control experiments were also conducted using only AO and
575 photolysis (UVC) in order to evaluate the effects of these processes on the degradation
576 of Sac. Ac. and on the formation of its intermediates (Fig. S-4).

577

578 **Fig. 5**. Analysis of salicylic acid (Sac. Ac.) and 2,3- and 2,5-dihydroxybenzoic acid
579 (DHBA) degradation as a function of time, based on the application of the following
580 treatment systems: **a)** AO/e-H_2O_2; **b)** AO/e-H_2O_2@e-ClO^-;**c)**UVC/e-H_2O_2; **d)** UVC/e-
581 H_2O_2@e-ClO^-.

582 As expected, the AO/e-H_2O_2 system recorded low $HO^{\bullet}$ production (Fig. 5a),
583 since the activation of H_2O_2 has very slow kinetics in the absence of UVC radiation
584 [37]. It is also worth noting that H_2O_2 can be decomposed into H_2O and O_2 at standard
585 temperature and pressure (see **Eq. 14**).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \textbf{Eq. 14}$$

586 After 90 min of electrolysis under the AO/e-H_2O_2 system, the concentration of
587 2,5-DHBA was found to be approximately 1.1 mg L^{-1} (~7.1 µmol L^{-1}); despite the low
588 degradation value recorded, the presence of $HO^{\bullet}$ explains the good rate of TOC removal
589 (9.5%) obtained compared to the other systems that had no UVC. It should be noted that
590 although the AO/e-H_2O_2@e-ClO^- condition (Fig. 5b) was not tested in TBT
591 degradation, it helps explain the role of chlorine electrogenerated species in the system
592 – through the scavenger test. The AO/e-H_2O_2@e-ClO^- system recorded a decrease of
593 17.8 mg L^{-1} in Sac. Ac. concentration after 90 min of electrolysis; essentially, this is
594 more than five times higher than that recorded for the AO/e-H_2O_2 system. The 2,5-
595 DHBA concentration was found to be 1.5 mg L^{-1} under the AO/e-H_2O_2@e-ClO^-

system; this value is quite close to that recorded for the AO/e-H_2O_2 system (Fig. 5a). This result, related to the formation of 2,5-DHBA, is found to be consistent with the AO/e-ClO^- system, which shows 33.7% of TBT degradation, but only 3.5% of TOC removal (see Fig. 4a-b). Importantly, these findings show that chlorine species favor the removal of contaminants, while hydroxyl radical favor TOC reduction.

In systems with UVC light, Sac. Ac. degradation is found to be more pronounced than in those without irradiation; this can be observed from the results obtained for the UVC/e-H_2O_2 and UVC/e-H_2O_2@e-ClO^- systems shown in Figs. 5d-c. In the control tests (Fig. S-4), one will observe that there is a decrease in Sac. Ac. concentration in the presence of only UVC light, but no intermediates are detected; this is attributed to the photolysis of the Sac. Ac. molecule and not to the effect of the $HO^{\bullet}$ species. Thus, it is necessary to keep in mind that in all the processes in which UVC is incorporated, a small portion of the decrease in Sac. Ac. is caused by the photolysis of the molecule.

As observed in the UVC/e-H_2O_2 and UVC/e-H_2O_2@e-ClO^- processes (Fig 5d-c), detecting the presence of 2,3 and 2,5-DHBA implies that $HO^{\bullet}$ species have been generated and are acting in the hydroxylation of Sac. Ac. The UVC/e-H_2O_2 system exhibited the formation of 2,3- and 2,5-DHBA, which apparently presented a plateau concentration after 60 min of electrolysis, reaching 10.1 and 7.3 mg L^{-1}, respectively, in 90 min. These results explain why the UVC/e-H_2O_2 system recorded excellent TBT removal and degradation rates (Fig. 4a-b). As can be noted, between 60 and 90 min of electrolysis, the TBT degradation rate changes very little (97.3 and 99.8%, respectively); however, the TOC removal rate doubles from 23.4 to 51.2%. Essentially, the results show that $HO^{\bullet}$ plays an important role in TBT degradation (see Fig. 4a-b).

Another interesting observation that is worth mentioning is that the results obtained for the UVC/e-H_2O_2@e-ClO^- system (Fig. 5d) provide insights into the generation of RCS in that system rather than only $HO^\bullet$ species. In 60 min of electrolysis, the concentration of 2,3 and 2,5-DHBA reached a plateau at 8.7 and 6.8 mg L^{-1}, respectively; within the span of this time, the TBT degradation and TOC removal rates recorded were 98.9% and 32.6%, respectively (see Fig. 4a-b). However, after 60 min of electrolysis, a decrease was observed in the concentration of both 2,3- and 2,5-DHBA compounds; this explains the preferred pathway of RCS, which is aimed at removing other compounds rather than mineralizing them.

It is worth highlighting that despite the role played by $HO^\bullet$, other mechanisms are involved in the UVC/e-H_2O_2@e-ClO^- process applied for TBT degradation (Fig. 6). The degradation of TBT in water also occurs via the action of reactive chlorine species (e.g. Cl_2, HClO/ClO^- and $Cl^\bullet$), as previously explained here. These RCS species are together responsible for the conversion of TBT into intermediates and/or inorganic ions, which leads to the partial mineralization of the molecule. For the mineralization process, a minor contribution is also expected from direct oxidation and UVC photolysis.

Fig. 6. Schematic diagram of possible TBT degradation mechanisms under the UVC/e-H_2O_2@e-ClO^- system.

3.4 Possible Pathway of TBT Degradation

To better understand the role of e-H_2O_2 and e-ClO^- oxidants combined with UVC irradiation in TBT degradation, the degradation by-products generated in the most efficient systems (UVC/e-H_2O_2, UVC/e-ClO^-, and UVC/e-H_2O_2@e-ClO^-) were detected and identified through LC–MS/MS analyses. The mass spectra of the

intermediates were recorded, and their structures were proposed through the analysis of the protonated ions $[M+H]^+$ and fragmentation patterns. As reported in the literature, the mass spectrum of TBT (molecular weight 228 Da) shows a protonated ion $[M+H]^+$, with *m*/*z* 229 and a fragment with *m/z* 172 [38]. Other fragments resulting from the cleavage between nitrogen and the carbonyl group include the thiadiazole ring (see Fig S-5).

The LC-MS chromatograms obtained for the UVC/e-H_2O_2, UVC/e-ClO^- and UVC/e-H_2O_2@e-ClO^- systems revealed the presence of 17 main intermediates in TBT degradation. This outcome was anticipated, given that the degradation curves and TOC analysis exhibited distinct responses for the three systems, as discussed in the previous section. Table S-1 presents the 17 intermediates recorded in the process involving the degradation of TBT under the specified systems. Based on the identified intermediates, four pathways for TBT degradation were proposed; these pathways are presented in Fig. 7.

Fig. 7. Possible pathways for TBT degradation based on the application of the UVC/e-H_2O_2 (navy blue arrow), UVC/e-ClO^- (red arrow) and UVC/e-H_2O_2@e-ClO^- (light blue arrow) systems.

Pathway 1 begins with the hydroxylation of the 1,3-dimethylurea group of TBT, which generates intermediate **1** with *m/z* 245. The validity of this route is corroborated by the presence of the fragment with *m/z* 172, corresponding to 5-*tert*-butyl-**N**-methyl-1,3,4-thiadiazol-2-amine. The hydroxylated product **1** undergoes oxidation, giving rise to compound **2**, which is characterized by a molecular ion with m/z 243 and m/z 265 $[M+Na]^+$. Compound **3** *(m/z* 229) is derived from the demethylation of compound **2**, which likely occurs through the oxidation of the methyl group in the urea group,

transforming it into a methylene group, followed by the hydrolysis and the loss of the formyl group ($H_2C=O$)[33,38,39].

The elimination of the terminal formaldehyde group in intermediate 2 is the proposed pathway for the formation of compound **4** with *m/z* 215 [38,39]. Compound **4** then undergoes the following processes: (i) hydroxylation of the central methyl, resulting in product **7** with *m/z* 231; subsequent hydroxylation in the *tert*-butyl group of compound 4 generates the derivative compound **8** (*m/z* 279); and (ii) cleavage of the N-C bond of the urea group, with the release of formamide, gives rise to compound **5** (*m/z* 172) [24,33,39]. The subsequent oxidation of the methyl substituent of N to alcohol in compound **5** gives rise to derivative compound **6** with *m/z* 174 [33].

A second identified degradation route (Pathway 2) begins with the hydroxylation of the central methyl group of TBT, which gives rise to compound **9** with *m/z* 245. This compound was identified based on the characteristic fragment with *m/z* 188, which is indicative of the rearrangement of primary amides described by McLafferty [24,39]. The hydroxylation of the *tert*-butyl group in compound **9**, followed by the subsequent oxidation of the alcohol substituent of N to an aldehyde, results in the formation of product **10** with *m/z* 291 [24].

A third possible TBT degradation route (Pathway 3) involves the hydroxylation of the *tert*-butyl group of TBT, which leads to the formation of compound **11** (*m/z* 245). The hydroxylation of the alkane group has been reported in studies on TBT degradation, with the characteristic fragment being *m/z* 184[38,39]. During the electrolysis conducted in the presence of Cl^-, we identified intermediate compounds **12** (*m/z* 265) and **13** (*m/z* 284), which are derived from organochlorination reactions. In compound **12**, chlorination occurs in the methyl of the tert-butyl group due to the higher reactivity of hydrogen atoms in alkanes. The conditions applied in the electrolysis can also induce

chlorination in the nitrogen of the amide group, leading to the formation of product **13** [24].

Pathway 4 is proposed based on the degradation and chlorination of the TBT molecule. Intermediate compound **14** (*m/z* 215) is derived from the elimination of a methyl group from the central nitrogen of the urea group. Degradation products **4** and **14** (both with *m/z* 215) have been previously reported in studies on TBT degradation; their structures were differentiated by the presence of fragments with *m/z* 172 and *m/z* 158, corresponding to the loss of formamide (45 Da) and methylformamide (59 Da), respectively [38]. Successive demethylations, chlorinations and hydrolysis of compound **14** generated the intermediates **15** (*m/z* 227), **16** (*m/z* 213), and **17** (*m/z* 199).

The proposed chemical structures indicate the following (Fig. 7; Table S-1): (i) in the processes involving the presence of peroxide ions in the treated solution, degradation products are formed through hydroxylation, oxidation and elimination reactions; (ii) in chlorine-involved processes, hydroxylation and oxidation of the methyl group (intermediates **1, 2, 3, 6-13**) are not observed, but one is able to identify the intermediates derived from the cleavage of TBT molecules and the organochlorinated compounds generated through the attack by Cl^- species on the anode surface or by electrogenerated active chlorine species; (iii) the electrolysis conducted in the presence of both chlorine and peroxide ions in the treated solution was the only process that led to the generation of hydroxylated organochlorine intermediates (**12** and **13**).

3.5 Toxicity Assessment of TBT and its Degradation By-products

Studies on the removal of organic pollutants from water commonly focus on the elimination of the target substance. However, assessing the degradation by-products and their toxicity is equally vital, as these substances can also negatively impact the environment. Chlorinated derivatives have been specifically demonstrated to exhibit

719 potential toxicity [40]; hence, in this study, a prediction analysis was conducted using
720 the Comptox tool to evaluate and predict the ecotoxicity profile of chlorinated TBT by-
721 products.

722 The Globally Harmonized System of Classification and Labeling of Chemical
723 Products (GHS) determines the classification of a substance based on its potential
724 hazard to the aquatic environment. This classification relies on the following: acute
725 toxicity data, such as lethal concentration 50% (LC_{50}) or effective concentration 50%
726 (EC_{50}); and chronic toxicity data, including no observed effect concentration
727 (NOEC)[41].

728 While experimentally derived test data are preferred, validated quantitative
729 structure-activity relationships (QSARs) for aquatic toxicity are accepted in the GHS
730 classification process [41]. GHS defines three categories for acute toxicity (very toxic,
731 toxic, and harmful), while for chronic toxicity, the same three acute categories are
732 employed together with category 4, which is associated with long-lasting harmful
733 effects. The classification relies on NOEC, or equivalent ECx data, in conjunction with
734 data on the degradability of the target substance, along with data on the bio-
735 concentration factor (BCF) or the n-octanol and water partition coefficient (K_{ow}). Table
736 3 presents the LC_{50} values recorded for fish (*Fathead minnow*) and crustaceans
737 (*Daphnia magna*), along with the BCF with log K_{ow}, for all the 17 by-products
738 intermediates formed during TBT degradation.

739 **Table 3**. Results obtained from the analysis of ecotoxicity (LC_{50}) in fish and *Daphnia*
740 *magna*, along with physical-chemical parameters recorded for TBT degradation by-
741 products.

Compound	**LC_{50} (mgL^{-1})**	**BCF**	**Log K_{ow}**

	Fathead minnow (96 h)	***Daphnia magna (48h)***		
1	59.1	64.80	4.00	1.05
2	22.98	18.87	8.00	1.79
3	21.9	49.41	5.87	1.46
4	80.99	14.24	4.64	1.40
5	56.67	18.52	11.21	1.80
6	78.52	28.98	7.98	1.14
7	99.63	55.18	3.62	0.42
9	58.67	58.62	3.61	1.00
8	18.84	52.90	3.34	1.34
10	13.72	58.69	2.26	1.64
11	44.24	42.95	3.72	0.94
12	61.93	48.15	4.64	0.91
13	22.05	14.84	5.92	1.37
14	61.13	29.41	4.75	1.53
15	50.55	73.87	8.81	0.86
16	43.75	52.72	9.29	0.64
17	43.02	23.82	20.77	0.56

The LC_{50} values obtained for *Fathead minnow* and *Daphnia magna* were within the range of $10.0 < LC_{50} \leq 100$; this shows that the substances belong to the acute category 3, which is classified as harmful to aquatic life. Regarding the chronic ecotoxicity data, the LC_{50} values, along with BCF $\geq$ 500, and/or if absent, log $K_{ow} \geq 4$ show that these compounds fall in the chronic toxicity 3 classification, which means they are harmful to aquatic life, with long-lasting effects. Although these results indicate the presence of hazardous substances in the water after treatment, the chlorinated derivatives formed are less toxic than TBT, which is classified under the GHS hazard classification framework as category 1; i.e., it is very toxic to aquatic life, with short and long-lasting effects [33]. Despite their low toxicity effects, chlorinated by-products may pose potential risks even in low concentrations. Interestingly, a review of the toxicological aspects of water treated using chlorine-based advanced oxidation processes concluded that the toxicity effect can be managed through some experimental

parameters [42]. For us to have a more comprehensive understanding of the toxicity of chlorine by-products, further in-depth analyses are needed.

Although the EAOP system proposed in this study reduced the acute toxicity levels of TBT, it is quite difficult to compare it with other results, as very few studies have performed acute toxicity analyses using electrochemistry-based systems for TBT degradation [43–45]. Only one study was found regarding TBT decontamination, which presented toxicity results after a multi-stage treatment involving coagulation-flocculation-settling and a photo-Fenton process; in the aforementioned study, the authors employed *Vibrio fischeri* inhibition tests for the assessment of acute toxicity, where they observed a reduction in toxicity from 100% to 43% after treatment [46]. In this regard, the present study brings novel contributions to the fore by performing toxicity tests for by-products formed during TBT degradation using an EAOP system.

4 Conclusion and Future Perspectives

This work demonstrated the effectiveness of the UVC/e-H_2O_2@e-ClO^- system for TBT degradation and mineralization in an electrochemical flow reactor. Based on the findings, the following conclusions can be drawn:

- Under the best experimental conditions (10 mA cm^{-2}, 10 mmol L^{-1} Cl^-, and pH 7), the TBT molecule was almost completely degraded, where a degradation rate of 99.5% was recorded in only 60 min of treatment. In addition, over 63.0% TOC removal was obtained in 90 min.

- The combined UVC/e-H_2O_2@e-ClO^- process was found (estimated) to consume low amount of energy (about 1.54 kWh g^{-1} TOC). The co-generation of

779 oxidants from both electrodes significantly enhanced TBT mineralization, leading to an
780 increase of 8.8% in efficiency compared to the individual systems.

781 • $HO^{\bullet}$ and chlorine species were identified as the main reactive species
782 involved in the TBT degradation mechanism. Also, a total of 17 by-products were
783 detected, and four degradation pathways were proposed.

784 • The results obtained from the ecotoxicity estimations conducted suggest
785 that the by-products generated in the TBT degradation process were less toxic than
786 TBT, though they were still harmful to aquatic life. However, it is worth emphasizing
787 that, while QSAR analyses provide valuable initial estimates of acute and chronic
788 toxicity, the toxicological responses of the treated matrix should be experimentally
789 assessed in future studies for us to have a more comprehensive understanding of the
790 toxicity of TBT degradation by-products.

791 Finally, the pollutant treatment method investigated in this work offers an
792 alternative approach for using electrical energy more efficiently in EAOPs, as the
793 simultaneous activation of oxidants generated at both the cathode and anode enhances
794 the degradation of organic contaminants under UV light. In addition, the treatment
795 approach implemented in the present study sought to explore the fundamental aspects
796 involving the application of electrochemical flow reactors and the underlying technical
797 feasibility. The findings of the study provide a proof of concept that can be scaled up for
798 industrial applications and bring useful contributions to the fore on the ongoing research
799 on pollutants degradation.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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