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**ENHANCED UV DIRECT PHOTOLYSIS AND UV/H₂O₂ FOR OXIDATION OF TRICLOSAN AND
IBUPROFEN IN SYNTHETIC EFFLUENT: AN EXPERIMENTAL STUDY**

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Abstract

This study aimed to evaluate the implementation of an advanced oxidation system based on UV radiation and UV/H₂O₂ for degradation of TCS and IBU in synthetic effluent. The assays occurred in a 2L reactor, protected from external light and equipped with a UV lamp ($\lambda = 254\text{nm}$). The effect of contaminant concentration, fractions of chemical species present, and mineralization were evaluated. In the UV/ H₂O₂ system, different concentrations of H₂O₂ were studied for oxidation of the contaminants. The kinetic experiments took place between 75 - 270 min of UV irradiation. The results showed > 99% oxidation of TCS in the direct photolysis system at pH 9.4 after 12 min. The degradation of IBU in the UV/H₂O₂ system, when 10mg L⁻¹ of H₂O₂ was used, obtained 97.39% oxidation. We obtained k' values of 0.189 min⁻¹ for TCS when its highest oxidation occurred, and k' values of 0.0219 min⁻¹ for IBU. The system was not able to completely mineralize the contaminants, presenting high values of TOC and COD after treatment, thus suggesting the occurrence of phototransformation.

Keywords: Advanced oxidation processes. Kinetics. Photodegradation. PPCP.

1. Introduction

Being classified as emerging contaminants, pharmaceutically active compounds, and personal care products (PPCPs) can present serious risks to the environment. The increasing population and life expectancy of people cause PPCPs to be continuously consumed and released into the environment, thus such contaminants need not be persistent in order to compromise ecosystems (Arnold et al. 2013; Rede et al. 2019).

Not only behavioral and longevity changes, but environmental changes are also causing numerous consequences to the environment. An example of this is the effects provided by the COVID-19 pandemic, such as reduced concentrations of pollutant gases (Wang and Su 2020) and improved water quality parameters (Yunus et al. 2020). However, several negative effects have also been noted.

The use of pharmaceuticals and personal care products to treat and prevent COVID-19 has significantly increased the presence of these substances in wastewater treatment plants (Espejo et al. 2020; Bandala et al. 2021; Guidony et al. 2021). These contaminants can be non-prescription drugs that combat common symptoms such as fever, in the case of ibuprofen (Jamerson and Haryadi 2020), and antimicrobial agents widely present in hand sanitizers such as triclosan (Guidony et al. 2021).

Ibuprofen (IBU, (RS)-2-(4-(2 methylpropyl)phenyl)propanoic acid) is a weak organic acid, highly bound to plasma albumin and extensively metabolized and excreted in the form of metabolites and their conjugates, having an elimination half-life of approximately two hours (Hersh and Dionne 2017). After administration, about 15% of the compound is excreted in the parental form and 26% and 43% in the form of hydroxyl-IBU and carboxy-IBU metabolites, respectively (Farré, Marinell; Pérez, Sandra; Kantiani, Lina; Barceló 2008). In the natural environment IBU poses several risks, such as oxidative stress in fish (Plhalova et al., 2017), and negative effects of rotifer survival and reproduction (Pérez 2016).

Triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy) phenol) is a broad-spectrum antimicrobial agent, and due to its great efficiency, it has been increasingly used in the formulations of soaps, toothpastes, and various skin and oral cosmetic products (Iovino et al. 2019; Gopalakrishnan et al. 2021). TCS is introduced into the natural environment mainly through the discharge of domestic effluents. Already in the environment, triclosan represents

a potential risk because of its ability to inhibit algal growth (Mohan and Balakrishnan 2019), toxic effects on invertebrates (Khatikarn et al. 2018), and increased microbial resistance (Drury et al. 2013), among other effects.

Ingested pharmaceuticals are excreted into the environment through animal and human urine and feces (Fang et al. 2012).. About 10-90% of administered doses of pharmaceutical and personal care products (PPCPs) are excreted from the human body in parent forms, and the remainder as metabolites and/or conjugated forms (Balakrishna et al. 2017).

Due to the wide use of TCS and IBU, these emerging contaminants are detected in natural environments, such as rivers, at concentrations of 3 - 68 ng L⁻¹ (Yang et al. 2015) and 0.59 - 1.4 µL⁻¹ (Amos Sibeko et al. 2019), also being found in wastewater treatment plants 443 - 1757 ng L⁻¹ (Mohan and Balakrishnan 2019) and 8612.9 - 1607.8 ng L⁻¹ (Kermia et al. 2016). A few of the physicochemical properties of TCS and IBU are presented in Table 1.

Advanced Oxidation Processes (AOPs) is a concept initially proposed by Glaze in 1987. They consist of methods that can be applied to the treatment of various compounds that are difficult to remove, as they chemically destroy numerous contaminants by generating strong oxidizing agents, such as hydroxyl radicals (HO•), which can attack and mineralize organic contaminants (Glaze et al. 1987; Coxa et al. 2021).

AOPs are considered powerful engineering solutions for processes that usually need to be integrated for the removal of different contaminants, since they reach numerous compounds of different concentrations in the same treatment system (Coxa et al. 2021). Among the main AOPs used for degradation of organic substances are Fenton processes, ozonation, electrochemical oxidation, and photochemical processes (Domingues et al. 2021).

Photochemical processes have low secondary pollution rates and low operating costs (Liu et al. 2018; Tan et al. 2021). Such processes are based on the supply of energy through radiation ($E\lambda = h\nu$) to a molecule, where the substance absorbs the energy photons and reaches specific levels of excited states, levels sufficient for the excitation of electrons and formation of free radicals that will act on the organic contaminant (Cuerda-Correa et al. 2020). In this study, the photochemical processes UV/H₂O₂ and direct UV photolysis were evaluated as final polishing technology for oxidation of TCS and IBU in synthetic effluent.

Table 1. Physical-chemical properties of TCS and IBU

Compound	Chemical Structure	Physical-chemical properties
Triclosan		Molar mass = 289.54g mol ⁻¹ pKa = 7.9 (Pemberton and Hart 1999) IUPAC name: 5-chloro-2-(2, 4-dichlorophenoxy) phenol Solubility in water: 12 mg L ⁻¹ a 20°C (Dhillon et al. 2015)
Ibuprofen		Molar mass = 206.283g mol ⁻¹ pKa = 4.9 (Luo et al. 2018) IUPAC name: (RS)-2-(4-(2-methylpropyl)phenyl) propanoic acid Solubility in water: 21mg L ⁻¹ at 25 °C (Friuli et al. 2018)

2. Materials and Methods

2.1. Reagents

Triclosan ($\geq 97.0\%$) and ibuprofen ($\geq 99.0\%$), used for chromatographic curves, were purchased from Sigma-Aldrich. LC-MS grade MeOH, formic acid (analytical grade) and ultrapure water ($> 18\text{ M}\Omega\text{ cm}$, Milli-Q-POD) were used for HPLC analyses. Triclosan ($\geq 97\%$, Êxodo científica, Brazil), commercial ibuprofen powder (Artesani, Brazil), NaOH and hydrogen peroxide (analytical grades) were used for the synthetic effluent. Na_2HPO_4 , KH_2PO_4 , Na_2CO_3 , NaHCO_3 , CH_3COOH and $\text{C}_2\text{H}_3\text{NaO}_2$ (analytical grades) were used for buffer solutions.

2.2. Quantitative Analyses

Quantitative analyses were performed using high-performance liquid chromatography (LCMS 2020, Shimadzu) with an SPD-M20A photodiode array detector. Separation took place on a C18 column (250 x 4.6 mm; 5 μm) operated at 30°C, using mobile phase in isocratic mode (80:20 MeOH and ultrapure water mixture, acidified with 0.001% formic acid) with flow rate of 0.8 mL min⁻¹, injection volume of 20 μL , and 25 min of analysis time. The wavelength was maintained at 200 and 280 nm for detection of IBU and TCS, respectively. Quantification was done through chromatographic curves updated periodically with standard solutions of TCS and IBU. The chromatographic detection limit was 0.05 and 0.1 mg L⁻¹ for TCS and IBU, respectively.

TOC concentration was determined by the difference of total carbon and inorganic carbon using a total organic carbon analyzer (TOC-L CPN, Shimadzu), with values reported as the average of three successive readings.

2.3. Synthetic effluent

The stock solution of triclosan uses a methodology adapted from Lu et al. (Lu et al. 2009), being the mass of triclosan dissolved in 20mL of NaOH 0.01 Mol L⁻¹, previously cooled. The volume was gauged with buffer solution. The stock solution of ibuprofen was adapted from Wang et al. 2019), formulated by dissolving the mass of IBU in 0.5mL of MeOH, due to the low solubility of the compound in water.

The synthetic effluent was made up from the solutions of triclosan and ibuprofen, and the pH was controlled by 10mM buffer solutions. Carbonate-bicarbonate buffer was used for pH = 9.4, phosphate buffer for pH = 6.0, and acetate buffer for pH = 3.6.

2.4. Experimental set-up

The reactor was made of glass with dimensions of 15cm x 45cm x 15cm, with the base established on two magnetic stirrers kept at 120 rpm. At the top, a UV lamp (OSRAM Puritec HNS L, Italy) of 38cm in length and 36W of power, average wavelength of 254nm, and average light intensity of 7800cd (Fig. 1). The reactor was installed in a dark room with no light entering from the external environment.

Fig. 1. Experimental set-up used for direct UV and UV/H₂O₂ oxidation of IBU and TCS in synthetic effluent.

2.5. Photo-oxidation experiments

The reactor operating conditions on the photo-oxidation of IBU and TCS were evaluated as a function of irradiation time (0 – 270 min). The direct photolysis experiments occurred by varying the parameters, initial concentration ($TCS_0 = 8.89 - 17.79 \text{ mg L}^{-1}$; $IBU_0 = 9.90 - 34.24 \text{ mg L}^{-1}$), and pH of the solution (pH = 3.6; 6.0; 9.4). The UV/H₂O₂ system was studied by adding H₂O₂ (0 – 15 mg L⁻¹), keeping the concentrations of IBU and TCS constant ($TCS_0 = 15.46 \text{ mg L}^{-1}$; $IBU_0 = 34.5 \text{ mg L}^{-1}$) and pH = 6.0. For all experiments the temperature was kept constant at $25 \pm 2^\circ\text{C}$. The UV lamp was turned on 30 min before the effluent was submitted to irradiation in order to reduce the variation of photon incidence due to the previous heating of the equipment.

3. Results and discussion

3.1. The effect of concentration on direct photolysis

The presence of different concentrations of IBU and TCS in liquid effluents justifies the need to understand the effect of this parameter on the degradation process.

The effect of the initial concentration of triclosan (TCS_0) and ibuprofen (IBU_0) on the photo-oxidation system is presented by Fig. 2, as a function of irradiation time. The experiments were developed using 2L of synthetic effluent at pH = 6.0, a value adopted respecting the limits for discharge of effluents into water bodies according to Brazilian federal regulations (Conama 2005).

For ibuprofen (Fig. 2a), when in initial concentration ($IBU_0 = 34.24 \pm 1.24 \text{ mg L}^{-1}$), the system showed an removal rate of 83.28% in 270 min with a remaining concentration of $5.73 \pm 0.16 \text{ mg L}^{-1}$. The reduction of the initial concentration led to a reduction of the remaining concentration. In terms of degradation efficiency, the highest value was achieved by the system with $IBU_0 = 24.77 \pm 0.51$, about 88.10%. Overall, the average efficiency was 82.63% among all experiments. Wang et al. (2019) in 90 min of irradiation using a UV-LED system reported 51.58% degradation using an initial concentration of 41.25 mg L^{-1} in 8mL, a value lower than that obtained by this study.

The system was not greatly affected by the concentration of IBU for values lower than $34.24 \pm 1.24 \text{ mg L}^{-1}$, where the difference between tests was $0.88 \pm 0.43 \text{ mg L}^{-1}$, which was lower than the final difference of $3.63 \pm 0.21 \text{ mg L}^{-1}$ obtained between the experiment with higher and lower concentration, thus revealing some effect on removal efficiency when high concentrations are used. Peng et al. (2017) attributed such behavior to the high

presence of intermediates, which hinder the oxidation reactions of IBU. Wang et al. (2019), employing concentrations of 41.26 – 103.14 mg L⁻¹, showed that the photo-oxidation rate of IBU is directly proportional to IBU₀, going against the results suggested by this present study, where concentrations ≥ 34.24mg L⁻¹ affect the removal efficiency of the direct UV photo-oxidation system.

TCS degradation (Fig. 2b) was not shown to be directly affected by TCS₀ up to 15.15 ± 0.84 mg L⁻¹, since in 60 min of exposure, about 99.5% of the concentrations TCS₀ = 15.15 ± 0.84 mg L⁻¹ and TCS₀ = 8.89 ± 0.83 mg L⁻¹ were degraded. However, concentrations above these values are shown to affect the degradation system, similar to the behavior exhibited by IBU. In the experiment with TCS₀ = 17.79 ± 0.44 mg L⁻¹, the degradation efficiency was 87.12% in 60 min, showing a remaining concentration of 2.29 ± 0.01 mg L⁻¹. Iovino et al. (2019), using a direct photolysis system at pH 6.0 and concentrations of 4.48 - 17.89mg L⁻¹ in 100mL concluded that 80% of the initial concentration was degraded in the first 5 min. Iovino et al. (2019), also reported a remaining concentration of 0.049mg L⁻¹ when TCS₀ = 7.78mg L⁻¹ in a direct photolysis system after 60 min of irradiation in 100 mL of solution. This value is lower than the one presented in this study, because when TCS₀ = 8.89 ± 0.83 mg L⁻¹ was used, values below the detection limit were obtained after 40 min of irradiation.

Fig. 1. The effect of initial concentration of (a) IBU and (b) TCS in synthetic effluent pH = 6.0 on oxidation by direct photolysis system.

3.2. The effect of chemical speciation on direct photolysis

The chemical speciation was evaluated by dissolving the contaminants in different pH ranges, respecting the *pKa* of each target pollutant. In general, the molecular species is favored when pH < *pKa*, as is the anionic species when pH > *pKa*.

The *pKa* = 4.9 (Pemberton and Hart 1999) and *pKa* = 7.9 (Luo et al. 2018) values were used for TCS and IBU, respectively. The fractions of anionic (α^-) and neutral (α) species of the target contaminants were determined according to Eq. (1) and Eq. (2), as proposed by Luo et al. (2018).

$$\alpha = \frac{10^{-pH}}{10^{-pKa} + 10^{-pH}} \quad (1)$$

$$\alpha^- = \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH}} \quad (2)$$

The behavior of IBU and TCS chemical fractions as a function of pH is shown in Fig.3

Fig. 3 Fraction of chemical species of (a) IBU and (b) TCS as a function of pH

For IBU, the experiments were performed at pH = 6.0 and 3.2, and 92.64% of the anionic species (IBU⁻) and 95.2% of the neutral species prevailed, respectively. For TCS, the experiments were performed at pH = 9.4 and 6.0, and 96.93% of the anionic form (TCS⁻) and 98.76% of the neutral form prevailed, respectively.

The obtained data show a higher efficiency of IBU⁻ degradation than IBU (Fig. 4a), with the contaminant being reduced by 83.2% in 270 min (Fig. 3a). Such results are in agreement with the values reported by Iovino et al. (2016), who observed the decrease of oxidation efficiency with decreasing pH, obtaining the lowest oxidation values near pH 3.

When compared to TCS, it is remarkable the greater difficulty of oxidation of the IBU molecule by the UV system. Such behavior can be justified by the difference between the chemical structures of the contaminants. The presence of certain functional groups such as phenol (Ar–OH), weak C–H bonds, and aryl chloride (Ar–Cl) in the TCS molecule can facilitate photochemical reactions stimulated by the direct absorption of ultraviolet radiation (Ahmad et al. 2016; Bartolomeu et al. 2018), while the IBU molecule presents only weak C–H bonds.

The oxidation of TCS using the direct photolysis system at pH 9.4 proved to be much more efficient (Fig. 4b), obtaining pH 98.73% oxidation in 10 min, and in 12 min the TCS concentration was already below the detection level of the chromatograph. When the experiments took place at pH 6.0, said result was only obtained between 60 and 100 min. The deprotonated form of TCS was shown to be more susceptible to degradation by direct photolysis than its molecular form. The rapid oxidation of TCS at pH > 9, as reported by this study, is in line with data obtained by Iovino et al. (2019), using a direct photolysis system in a 100mL reactor at pH 10, achieving nearly 99% removal in less than 30 min.

When compared to pH 6, the anionic form of the TCS molecule was shown to be more efficient for degradation (Fig. 4b). It is suggestive to state that this process occurred due to the percentage of deprotonated

anions of the phenol group present in the synthetic effluent, which is affected with increasing pH, thus increasing the molar absorption coefficient (Huang et al. 2018).

Fig. 4. The effect of chemical speciation on the temporal degradation of (a) IBU pH = 6.0 and 3.2 and (b) TCS pH = 9.4 and 6.0 in synthetic effluent by the direct UV photolysis system. $IBU_0 = 29.61 \pm 0.59 \text{ mg L}^{-1}$, $TCS_0 = 15.10 \pm 0.43 \text{ mg L}^{-1}$

3.3. The effect of H₂O₂ on the UV/H₂O₂ system

Photoassisted peroxidation was evaluated using different concentrations of H₂O₂ in synthetic effluent containing IBU and TCS at pH = 6.0 and room temperature (25 ± 2°C). Concentrations of 15, 10, and 5 mg L⁻¹ of H₂O₂ were used. The use of H₂O₂ aims to increase the speed of degradation of the target contaminants through oxidation by •OH radicals arising from photolytic cleavage of the H₂O₂ molecule (Eq. 3).

The hydroxyl radical is a strong, non-selective oxidizing agent that acts on the oxidation of organic and organometallic pollutants present in the solution, thus leading to their mineralization in the forms of inorganic ions, H₂O or CO₂ (Cuerda-Correa et al. 2020).

The low oxidation rate of IBU by the direct photolysis system justifies the use of H₂O₂ as an oxidizing agent, acting in tandem with UV radiation in the UV/H₂O₂ system. The results show a reduction in the degradation time of the contaminant when compared to the direct UV system at pH 6.0. The time reduction was 195 min when using the lowest concentration of H₂O₂ (5 mg L⁻¹) and 225 min when using the highest concentration of H₂O₂ (15 mg L⁻¹).

The highest efficiency for IBU oxidation was obtained when 10 mg L⁻¹ of H₂O₂ was used, resulting in 97.39% oxidation of the contaminant after 75 min (Fig. 5a). The use of 15 and 5 mg L⁻¹ of H₂O₂ resulted in 95.38% and 82.32% oxidation, respectively. Peng et al. (2017) reported 82.4% removals of IBU in 30 min UV/H₂O₂ system when using 20 mg L⁻¹ and 15 mg L⁻¹ of IBU in 200 mL and 75W lamp. In the present study, 30 min of irradiation and 34.5 mg L⁻¹ of IBU obtained 72.03% oxidation of the target contaminant in the system with 15 mg L⁻¹ of H₂O₂.

Unlike IBU, when compared to the direct photolysis system at pH 9.4, the oxidation of TCS by UV/H₂O₂ did not prove to be the superior reactor among those used in this study. The results obtained for degradation of TCS by UV/H₂O₂ showed that the efficiency is inversely related to the concentration of H₂O₂ used, with lower concentrations being the source of higher oxidation rates. Using 5 mg L⁻¹ of H₂O₂ degraded 97.69 % of TCS in the synthetic effluent in 15 min and found below the detection limit between 15 and 30 min of irradiation. By increasing oxidant concentration, using 10 and 15 mg L⁻¹ of H₂O₂, TCS was below the detection limit only between 30-60 min and between 60-75 min, respectively.

H₂O₂ was not shown to be fully decomposed by the system, and its residual was found in all treatments. For the experiments using 15, 10, and 5 mg L⁻¹ of H₂O₂, after 60 min, a residual of 10, 5, and 5 mg L⁻¹ of H₂O₂ in the synthetic effluent was still present. Liu et al. also reported a delay in H₂O₂ consumption in the UV/H₂O₂ system, being consumed by 20% after 10h using 17 mg L⁻¹ of H₂O₂ (Liu, Yiqing; He, Xuexiang; Fu, Yongsheng; Dionysiou 2016).

Fig. 5. The effect of the presence of H₂O₂, 15, 10, and 5 mg L⁻¹ on the temporal degradation of (a) IBU and (b) TCS in synthetic effluent pH = 6.0 by the UV/H₂O₂ system. IBU₀ = 34.5 ± 0.25 mg L⁻¹, TCS₀ = 15.46 ± 0.31 mg L⁻¹.

3.4. Pseudo-first order kinetics and t_{1/2}

The degradation kinetics were fitted to the pseudo-first order model. The pseudo-first order rate (k' , min⁻¹) is obtained from Eq. (4), and can also be observed from the slope of the curve of ln(C_t/C₀) by t .

$$-k' t = \ln \left(\frac{C_t}{C_0} \right) \quad (4)$$

Where t is the photochemical oxidation time (min); C_t is the concentration at any instant t (mg L⁻¹); C_0 is the initial concentration (mg L⁻¹); and k' is the pseudo-first order rate (min⁻¹).

The photochemical degradation half-life was obtained from Eq. (5) according to Luo et al. (2018).

$$t_{1/2} = \frac{\ln 2}{k'} \quad (5)$$

Where $t_{1/2}$ is the degradation half-life (min) and k' is the pseudo-first order rate.

Figure 5 presents the degradation kinetic models of IBU and TCS fitted to the pseudo-first-order model at different pH values (pH = 3.6; 6.0; 9.4) and H_2O_2 concentrations (5, 10, and 15 mg L^{-1} ; pH = 6.0) presenting as a fixed parameter the initial concentration of the target contaminants. Table 3 lists the constants and degradation half-lives of TCS and IBU.

The degradation constant k'_{TCS^-} was higher than k'_{TCS} . It was observed that the target contaminant was degraded faster when the pH values increased from 3.6 to 9.4 (Fig. 6b). For IBU the same behavior was observed (Fig. 6a), where the degradation constant k'_{IBU^-} was higher than that obtained when the contaminant was in its neutral molecular form. As the pH is increased, the neutral form deprotonates in solution, occurring the increase of k' for IBU, as can be observed the values of the constants at pH 3.6, 6.0, and 9.4 (Table 2). This same behavior was observed by Luo et al. (2018), in which the constant at pH 7.55 was higher than that at pH 3.0 in the degradation of IBU by direct photolysis.

For TCS, the chemical speciation showed that the direct UV photolysis system at pH 9.4 is more efficient in the photo-oxidation of the contaminant, which is confirmed by the obtained values of k' and $t_{1/2}$ (Table 2). Azarpira et al. (2019) reported degradation constants of 0.131 and 0.0687 for TCS at concentrations of 7.5 and

291 10.0 mg L⁻¹ in a UV/Iodide/ZnO (UIZ) degradation system with 11W lamps in 150mL of solution.

Fig. 6. Degradation kinetics by UV systems at pH = 9.4, 6.0 and 3.6, for (a) IBU and (b) TCS and UV/H₂O₂ with [H₂O₂] = 15, 10 and 5 mg L⁻¹ at pH 6.0 for (c) IBU and (d) TCS. TCS₀ = 15.46 ± 0.31 mg L⁻¹, IBU₀ = 34.5 ± 0.25 mg L⁻¹. The lines represent the pseudo-first order model.

Sanchez-Prado et al. (2006), in a study on the photodegradation of TCS in domestic wastewater using UV and solar radiation, found that the $t_{1/2}$ for degradation of the contaminant was 4.8 min at pH around 7, with the pollutant being mostly in its molecular form. Such a result points to the reverse of that reported in this study, in which the contaminant in its molecular form (pH 6.0 and 3.6) showed longer degradation half-lives both in the absence of H₂O₂ and in the presence of it (Table 2). This difference in results presented by Sanchez-Prado et al. (2006) can be explained by the use of a real matrix, where it is possible to occur the interference of different substances present in solution, and even the acceleration of degradation through organic matter, as reported by Iovino et al. (2019) using humic acids as a model compound of natural organic matter in the degradation of TCS by UV radiation.

The system used for IBU oxidation showed large degradation half-lives in the absence of H₂O₂ (Table 2). This may be related to the high concentration of IBU used. According to Peng et al. (2017), in an experiment using concentrations of 5 – 25 mg L⁻¹ of IBU, increasing the concentration hindered the oxidation process, since the high

concentration of IBU in solution also means the existence of high concentrations of intermediates. These intermediates act as scavengers for OH radicals, reducing the reaction of the oxidant with IBU. Peng et al. further concluded similar results to those presented by the present study, such as the difficulty of oxidation of IBU by UV radiation alone (Peng et al. 2017).

Table 2. Pseudo-first order kinetic constants and half-lives of TCS and IBU in synthetic effluent in different UV and UV/H₂O₂ direct photolysis reactors. TCS₀ = 15.46 ± 0.31 mg L⁻¹, IBU₀ = 34.5 ± 0.25 mg L⁻¹.

IBU			TCS			Operational conditions
<i>k'</i> (min ⁻¹)	R ²	t _{1/2} (min)	<i>k'</i> (min ⁻¹)	R ²	t _{1/2} (min)	
0.0031	0.994	223.60	0.189	0.998	3.66	Direct photolysis pH 9.4
0.0029	0.998	239.01	0.0799	0.970	8.67	Direct photolysis pH 6.0
0.0013	0.991	533.19	0.0911	0.982	7.61	Direct photolysis pH 3.6
0.0175	0.999	39.61	0.0863	0.979	8.03	UV/H ₂ O ₂ (15mg L ⁻¹) pH 6.0
0.0219	0.996	31.65	0.0834	0.979	8.31	UV/H ₂ O ₂ (10mg L ⁻¹) pH 6.0
0.0097	0.996	71.46	0.108	0.993	6.42	UV/H ₂ O ₂ (5mg L ⁻¹) pH 6.0

The comparison between the pseudo-first order rates reported by the scientific literature is presented by Table 3 for both TCS and IBU under different operating conditions.

Table 3. Kinetic constants: comparison of the literature

TCS ₀ (mg L ⁻¹)	IBU ₀ (mg L ⁻¹)	<i>k'</i> (min ⁻¹)	pH	Operational conditions	Ref.
10.0	0	0.0687	7.0	UIZ system; 11W low pressure mercury lamp	(Azarpira et al. 2019)
7.5	0	0.1313	7.0		
5.0	0	0.1882	7.0		
7.8	0	0.302	6.0	Direct photolysis; 5 tubes 8W, $\lambda = 254\text{nm}$	(Iovino et al. 2019)
1.0	0	0.0045	7.0	Direct photolysis; pure water; sunlight	(Qiao et al. 2014)
1.0	0	0.0019	9.0	Direct photolysis; pure water; 500W xenon lamp	
1.0	0	0.0108	7.0	Direct photolysis; pure water; 500W Hg lamp	
0	2.1	0.0043	3.0	Direct photolysis; 10W low-pressure Hg lamp; $\lambda = 254\text{nm}$	(Luo et al. 2018)
0	2.1	0.0263	7.55		
0	15.0	0.0362	6.82	UV/H ₂ O ₂ ; H ₂ O ₂ = 0.6mM; pure water; 75W Hg lamp; $\lambda = 254\text{nm}$	(Peng et al. 2017)
0	5.0	0.037	-	Direct UV-C photolysis; pure water; three 9W UV-C lamps; $\lambda = 254\text{nm}$	(Da Silva et al. 2014)
0	5.0	0.001	-	Direct UV-A photolysis; pure water; three UV-A 9W lamps; $\lambda = 360\text{nm}$	
0	5.0	0.054	-	UV-C/TiO ₂ ; TiO ₂ = 120 mg L ⁻¹ ; pure water; three UV-C 9W lamps; $\lambda = 254\text{nm}$	

3.5. Mineralization

Despite the high oxidation rates of TCS and IBU obtained in this study, the results for TOC and COD showed that the contaminants were not entirely mineralized by the direct photolysis and UV/H₂O₂ systems. For the multicomponent direct photolysis system, the highest mineralization rate obtained was 47.27% at pH 9.4 after 270 min of irradiation time for TOC removal. In the UV/H₂O₂ system, 10.97% TOC removal was obtained using 15 mg L⁻¹ of H₂O₂ in multicomponent solution after 75 min. The substantial difference in oxidation may be directly related to the irradiation time and the pH of the solution. In more alkaline ranges the presence of anionic species facilitates the oxidation of IBU and TCS, and thus may enhance the mineralization of the contaminants.

The higher mineralization of contaminants by the direct UV system was also proven by the COD (Supplementary File). The experiments in UV/H₂O₂ system occurred at pH = 6.0, where even though the IBU was mostly in anionic form, the system showed low removals of TOC, due to the very difficult oxidation of IBU, the competition for •OH by the contaminants and the formation of intermediates. In pH 6.0 system TCS obtained 40.63% of TOC removal after 75 min, while for IBU about 10.26% was obtained.

Trousil et al. (2018) also obtained low TOC removal values for IBU degradation, about 20.37% in direct photolysis system and 30.09% in UV/TiO₂ system after 1h irradiation. The removal of TOC in the oxidation of IBU may be related to the continuous formation of small carboxylic acids during the process (Szabó et al. 2011).

The low mineralization data point to byproduct formation from the oxidation of TCS and IBU by both the direct photolysis system and the UV/H₂O₂ system. TCS has been known for its high rate of byproduct formation by phototransformation (Apell et al. 2020). Huang et al. (2018) draw attention to non-removal of byproduct cytotoxins by the UV and UV/H₂O₂ processes applied in the oxidation of TCS, even when reduction of the target contaminant concentration occurs, and increased UV fluence is required.

The main photolysis byproducts of IBU and TCS reported in the literature are shown in Fig. 7. For TCS, some byproducts formed are 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) arising from the skeletal rearrangement of the molecule, 2,4-dichlorophenol (DCP) formed from the cleavage of the ether (R-O-R), and 4'-chlorophenoxyphenol (4'-CIPP) from hydrodechlorination (Kliegman et al. 2013; Apell et al. 2020), where due to the use of MeOH as a cosolvent, the formation of 2-phenoxyphenol (PP) is facilitated (Apell et al. 2020). For IBU, it has been widely reported that decarboxylation occurs (Szabó et al. 2011; Luo et al. 2018). Also, hydroxylation to the benzene ring under high energy absorptions is possible (Luo et al. 2018; Wang et al. 2021). Some byproducts are 1-ethyl-4-(2-methylpropyl)-benzene, 1-(4-isobutylphenyl)ethanol, and 4-isobutylacetophenone (Szabó et al. 2011; Wang et al. 2021).

Fig. 7. Byproducts of degradation by direct photolysis proposed in the literature for (a) TCS (Kliegman et al. 2013; Apell et al. 2020) and (b) IBU (Szabó et al. 2011; Wang et al. 2021).

3.6. Electric energy per order (E_{EO})

The E_{EO} is a parameter used to evaluate the amount of energy required for the decay of the target contaminant concentration by order of magnitude a 90% reduction in 1 m³ of water (Keen et al. 2018). The figure of merit was calculated according to Bolton et al. (2001) and is represented using Eq. (6) and fitted to pseudo-first order kinetic behavior (Eq. 7).

$$E_{EO} = \frac{P \times t \times 1000}{V \times \log(C_0 / C_f)} \quad (6)$$

$$E_{EO} = \frac{38.4 \times P}{V \times k'} \quad (7)$$

Where E_{EO} is the electrical energy per order (kWh m⁻³ order⁻¹), P is the lamp power (kW), t is the time required for degradation (h), V is the solution volume (L), C_0 and C_f are the initial and final contaminant concentrations (mg L⁻¹), and k' is the pseudo-first order rate (min⁻¹).

Table 4 shows the E_{EO} values obtained under different operating conditions of the photochemical reactors employed for the degradation of IBU and TCS in synthetic effluent at different pH values and H₂O₂ concentrations. The low energy required for TCS degradation compared to IBU is remarkable. The lower E_{EO} values for TCS were already expected, since this contaminant proved to be more photosensitive than IBU.

The low E_{EO} value found in the direct photolysis system at pH 9.4 for TCS may be related to the wide presence of the TCS⁻ species in the solution. As discussed earlier, photochemical transformations occur more easily on the deprotonated anionic form of this contaminant. Due to the high interaction of TCS with ultraviolet radiation, the chemical bonds are more susceptible to direct exposure and thus all of them can be broken (Azarpira et al. 2019).

The presence of H₂O₂ in the reactor did not significantly reduce the energy required for oxidation of TCS, with the chemical speciation of the contaminant being much more significant. The chemical speciation showed that the greater presence of deprotonated species reduced the amount of energy required by 51.77%, when compared to pH 3.6 where there is a majority of the molecular form of the target substance.

Azarpira et al. (2019), using a UV/Iodide/ZnO-based advanced oxidation system (UIZ) in a 150mL tubular photochemical reactor and an 11W power UV lamp achieved E_{EO} values in range of 2.48 – 12.29 kWh m⁻³ order⁻¹ for TCS degradation between 1 and 10 mg L⁻¹. These values reported by Azarpira et al. (2019) are lower than those developed by this present study, where in a larger volume of effluent, it was possible to reach lower amounts of energy required for TCS degradation, thus implying cost reduction for oxidation of such contaminants through a simpler system of operation, when compared to a tubular reactor, and without the need to use chemical catalysts.

For IBU degradation, the photochemical system showed the need of H₂O₂ for E_{EO} reduction. IBU proved to be difficult to remove using the direct photolysis system, becoming more expensive when compared to TCS oxidation, requiring longer irradiation times and thus greater use of electricity. The use of 15 mg L⁻¹ of H₂O₂

reduced the energy required for IBU degradation by 82.29%. Although the use of H₂O₂ means implementing yet another cost to the system, the high reduction in energy use for degradation and the low concentration of H₂O₂ makes the cost of the oxidant less significant.

Trousil et al. reported E_{EO} of 136.2 kWh dm⁻³ using 11W power UV lamp in a volume of 20dm⁻³ and a concentration of 20mg dm⁻³ of IBU in a recirculating reactor. When using the UV/H₂O₂ system with concentration of 0.5 g dm⁻³ of oxidant, the energy required for degradation of 90% of the contaminant went to order of 61.2 kWh dm⁻³, a 55.1% reduction in energy consumption (Trousil et al. 2018).

Table 4. E_{EO} required for degradation of IBU and TCS in synthetic effluent by direct photolysis and UV/H₂O₂ systems. TCS₀ = 15.46 ± 0.31 mg L⁻¹, IBU₀ = 34.5 ± 0.25 mg L⁻¹

IBU	TCS	Operational conditions
E _{EO}	E _{EO}	
(kWh m ⁻³ order ⁻¹)	(kWh m ⁻³ order ⁻¹)	
222.97	3.66	Direct Photolysis pH 9.4
238.34	8.06	Direct Photolysis pH 6.0
531.69	7.59	Direct Photolysis pH 3.6
39.50	8.01	UV/H ₂ O ₂ (15 mg L ⁻¹) pH 6.0
31.56	8.28	UV/H ₂ O ₂ (10 mg L ⁻¹) pH 6.0
71.26	6.40	UV/H ₂ O ₂ (5 mg L ⁻¹) pH 6.0

4. Conclusion

In this study, the degradation of TCS and IBU was evaluated using two photochemical oxidation systems. The processes in direct photolysis and UV/H₂O₂ obtained favorable results for implementation as final polishing technology, indicating the use of direct photolysis at pH = 9.4 for TCS oxidation and the increment of H₂O₂ for IBU. The direct photolysis system at pH 9.4 obtained values below the detection level of the chromatograph after 10 min, the lowest E_{EO}, and the highest *k'* value, which was the best result obtained for TCS degradation. The UV/H₂O₂ system for oxidation of IBU reduced the E_{EO} values and the time required for concentration decay. About 97.39% of the contaminant was oxidized when 10mg L⁻¹ of H₂O₂ was used in 75 min of irradiation. The results point to incomplete mineralization of the target contaminants after both UV and UV/H₂O₂ treatments. About 10.75% was mineralized in the reactor with 10mg L⁻¹ of H₂O₂ and 47.27% in direct UV photolysis reactor pH 9.4, thus proving the formation of degradation byproducts, which can lead to toxic substances.

Declarations

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Conflict of Interest: The authors declare that they have no conflict of interest.

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565 **Graphical Abstract**

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