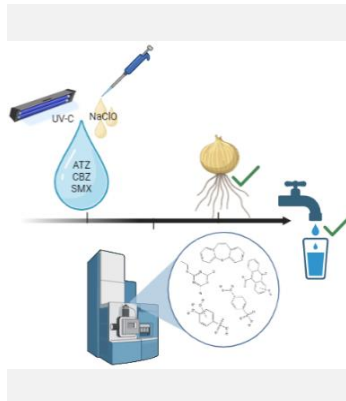


Advanced UV-C/Cl oxidation as an alternative for emerging contaminants removal on potabilization treatment plants

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Emerging contaminants (ECs) are increasingly found in drinking water due to the inefficiency of removal in potabilization treatment plants. Thus, this study aimed to apply the advanced oxidation process (AOPs) like UV-C/Cl for the degradation of atrazine (ATZ), carbamazepine (CBZ), and sulfamethoxazole (SMX). Degradation, transformation products (TPs), and toxicity were monitored. ATZ and SMX were removed in the combined process, while CBZ did not. The identification of suspected compounds was carried out by comparing experimental data with a database containing MS/MS information on 60 TPs previously identified in the literature studies which used AOPs ATZ, CBZ, and SMX degradation. The identified TPs showed different levels of toxicity via *in silico* assessment, while *in vivo* tests with *A. cepa* indicated the removal of toxicity after UV-C/Cl treatment. The results suggest the potential use of UV-C/Cl after enhancement in potabilization treatment plants to provide safer water to the population.

Introduction

ATZ, CBZ and SMX are among the ECs in treated water distributed for human consumption [1, 2, 3]. It is known that conventional water treatments are not capable of effectively removing trace of this ECs, requiring application or supplementation with advanced methods [4].

The advanced oxidation processes (AOPs) has the ability to degrade ECs via *in situ* generation of the hydroxyl radical (HO^\bullet) [5, 6]. Other oxidants and radicals may be involved in AOPs, such as reactive chlorine species (RCS), which can be obtained by combining photolysis with chlorination (UV/Cl) [7, 8]. Therefore, developing methods for ECs removal that can be easily implemented in existing potabilization treatment plants is an important issue for public health. Considering that Cl and UV-C are commonly employed in the disinfection stage of potabilization treatment plants, this study aimed to investigate the degradation of multicontaminants by UV-C, Cl, and the combined UV-C/Cl process. The presence of TPs was confirmed by evaluating the mass accuracy (± 5 ppm); adequacy to the isotopic standard in relation to the molecular formula of the precursor ion (mSigma) and the presence of diagnostic ions (fragments). and *in silico* toxicity were also evaluated.

Material and Methods

A complete 2^{k-p} factorial design was implemented with 3 factors, including a central point, and conducted in duplicate to define the optimal operating conditions (free chlorine concentration, solution flow rate, and presence/absence of UV-C radiation) using Minitab 17 software.

In the subsequent stage, the best conditions were applied to a new series of experiments to assess contaminant degradation, and degradation kinetics,

and to identify the generated transformation products, as well as the level of *in silico* toxicity.

The working solution comprised the contaminants ATZ, CBZ, and SMX diluted to a concentration of 5 mg L^{-1} each in deionized water. The treatment system consisted of a 2.0 L capacity reservoir connected to an axial UV-C reactor. The solution flow between the reservoir and the UV-C reactor was kept constant by a pump. Sodium hypochlorite 1% was manually and directly added to the reservoir at time zero. Samples were collected from the return hose to the reservoir at 0, 2.5, 5, 10, 15, 30, and 60 minutes.

The monitoring of EC removal was performed via high-performance liquid chromatography. Identification of transformation products was obtained by analyzing the treated sample under the best condition at 60 minutes using LC-QTOF-MS, followed by data processing in the TASQ® program. An *in silico* method using the OSIRIS® Property Explorer program was applied to correlate the data from LC-QTOF-MS to the mutagenic, tumorigenic, and irritating risk. Acute *in vivo* toxicity using *Allium cepa* as a test organism was used to complement the results of *in silico* toxicity.

Results and Discussion

From the degradation data of EC under different conditions, it was evident that the UV-C factor is essential for the removal of ATZ and SMX (Fig 1). The use of chlorine alone, at low or high concentrations (0.5 or 5.0 mg L^{-1}), is not capable of degrading the EC. Additionally, CBZ does not significantly degrade under any of the conditions tested.

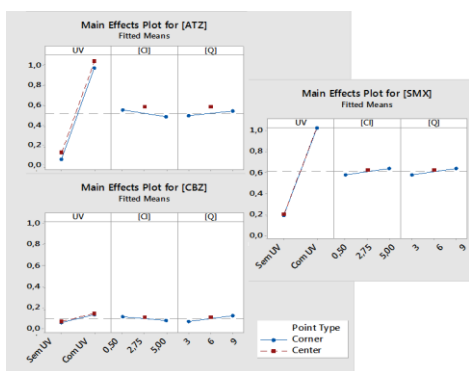


Figure 1. Main effects plot for the degradation of ATZ, CBZ, and SMX.

In the subsequent stage, the optimal parameters were applied in a new round of experiments. As a result, total degradation of ATZ and SMX was achieved (Fig. 2). The degradation of ATZ by the combined process can be attributed to the generation of HO[•] and RCS [11]. In contrast, SMX demonstrated high photosensitivity and reactivity with RCS [10, 11].

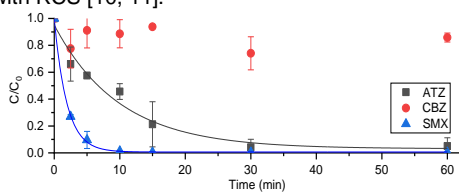


Figure 2. Degradation results of contaminants ATZ, CBZ, and SMX under optimal UV-C/Cl treatment conditions ([Cl⁻] = 0.5 mg L⁻¹ and recirculation flow rate of 1.9 L min⁻¹).

CBZ was not removed under any of the conditions, considered photorefractory and with low reactivity towards RCS. According to the literature, CBZ is

Conclusions

The results demonstrated that the UV-C/Cl method was capable of partial degrading of ATZ and SMX, but not CBZ. The main TPs of ATZ were present (DIA, DEA and HAZ), and the main TPS for CBZ and SMX, and more 3 TPs not identified (TP10, 3 and 8). Process improvement should be conducted to maximize the degradation of these ECs. Despite the formation of some toxic transformation products, it was also possible to remove the acute toxicity of the sample composed of the three contaminants. Further process conditions and analyses are being conducted for future application in conventional water treatment plants, aiming to enhance EC removal from treated water.

Acknowledgments

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reactive only with HO[•] and ozone [10, 11, 12]. It is possible that the irradiation of HOCl formed more RCS than HO[•], as there was the degradation of ATZ but not CBZ.

The Transformation Products (TP) identified post-treatment, as well as results from the *in silico* toxicological analysis, are presented in Table 1. Despite the formation of TP with high toxicity, such as some derivatives of ATZ and SMX, *in vivo* analysis with *A. cepa* indicates the removal of solution toxicity post-treatment. In other words, post-treatment samples exhibited statistically comparable root growth to the control, indicating toxicity removal after UV-C/Cl treatment.

Table 1. Transformation products identified in the post-treatment sample and toxicities were determined via *in silico* analysis.

Compound/transformation product (TP)	Toxicity risks *		
	M	T	I
Atrazine	Red	Red	Red
2-Chloro-4-ethylamino-6-amino-s-triazine (DIA)	Red	Red	Red
2-Chloro-4-amino-6-isopropylamino-s-triazine (DEA)	Red	Red	Red
2-hydroxyatrazine (HAZ)	Yellow	Green	Green
Carbamazepine	Red	Green	Green
Hydroxyl-CBZ	Green	Green	Green
TP252-B (Hydroxyl-CBZ isomer)	Green	Green	Green
CBZ-EP (Hydroxyl-CBZ isomer)	Yellow	Green	Green
Iminostilbene	Green	Green	Green
hydroxy-(9H,10H)-acridine-9-carbaldehyde	Yellow	Green	Green
9-hydroxy-acridine	Yellow	Green	Green
Sulfamethoxazole	Green	Green	Green
4(hydroxyamino) benzenesulfonic acid	Red	Yellow	Red
TP10	Green	Green	Green
TP 3	Red	Green	Red
TP8	Green	Green	Green

* M: mutagenic, T: tumorigenic, and I: irritant risks.