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The Impact of Antibiotics in Aquatic Environments and the Efficacy of Fenton-Based Processes for Their Removal

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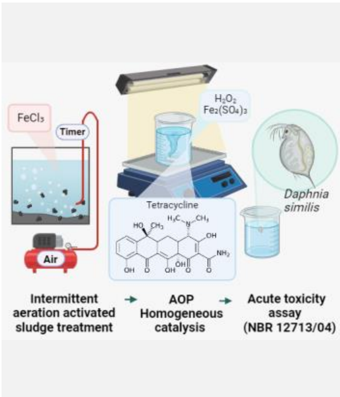

The antibiotic known as tetracycline (TC) is commonly found in various water sources, posing a serious threat to the health of aquatic organisms. In addition, antibiotics have been challenging to remove through biological processes. To improve the removal of TC, the advanced oxidative process Solar-Fenton-based process was proposed. In this study, the degradation of TC was examined using the solar direct photolysis, Solar/H_2O_2, Fenton and Solar-Fenton for synthetic solutions and real sludge. Regarding removal efficiency the process follows the order Solar-Fenton > Solar/H_2O_2 > Fenton > Solar. Acute toxicity assays with *Daphnia similis* indicated that the application of Fenton provided an increase of 3000-fold in the toxic unit for both matrices evaluated.

Introduction

Antibiotics in aquatic environments tend to bioaccumulate in the food chain, negatively affecting human health, with side effects such as endocrine disruption, mutagenicity, joint disease, central nervous system dysfunction, nephropathy, and altered photosensitivity [1]. Tetracycline (TC) concentrations have been identified in the range of de ng L^{-1} to µg L^{-1} in water bodies such as surface water, groundwater, and drinking water, as well as sediments and sludge [2]. Tetracycline residues have been detected at levels of 0.11 µg L^{-1} in surface water and 0.17 µg L^{-1} in effluents in the United States [3]. Given this, the removal of antibiotics in effluents via advanced oxidative processes (AOPs) via a Fenton-based process (**Eq. 1 to 5**) has shown satisfactory efficiency [4][5][6].

$$H_2O_2 + hv \rightarrow 2HO\bullet \quad (1)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^- \quad (2)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (3)$$
$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO\bullet + H^+ \quad (4)$$
$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (5)$$

In this sense, this study aims to evaluate the degradation efficiency of tetracycline (TC) in secondary effluent employing Fenton'-Based treatments and to assess acute toxicity after advanced treatment.

Material and Methods

Reagents. Tetracycline (TC, 98.0%-102.0%, 444.4 g mol^{-1}), molecular formula $C_{22}H_{24}N_2O_8$ was provided by Sigma-Aldrich. Acetonitrile (HPLC grade, Sigma-Aldrich), H_2SO_4 (97%), $FeSO_4 \cdot 7H_2O$, and acetic acid 99% (Lab Synth). Water was obtained from a Milli-Q Direct-Q (Millipore) system. Other chemicals used to adjust the pH of the solution were 0.1 mol L^{-1} NaOH and H_2SO_4.

Study area. The São Paulo Metropolitan Region, Brazil's largest urban agglomeration, contributes over 30% to the country's GDP. The selected wastewater treatment plant for this study was Barueri (-23.5125814, -46.848718). Employing refrigerated automatic samplers (Etsus 2000) the composite samples (24-hour) were analyzed for physicochemical characterization. The sample was previously treated via intermittent aeration-activated sludge treatment with a TDH of 12 hours, intermittent aeration of 20 minutes, and a concentration of 70 mg L^{-1} ferric chloride ($FeCl_3$).

Analytical methods. The study used ultra-fast liquid chromatography (UFLC, Shimadzu) to monitor TC concentrations with 30% acetonitrile and 70% water, and detected at 276 nm. The acute toxicity was evaluated using *Daphnia similis* [7].

Photocatalytic degradation. The photodegradation assays were performed using a mercury iodide lamp (Master HPI-T Plus, Philips Co.), providing 4.29 mW cm^{-2} in the range 290-800 nm. Sludge and synthetic solution with TC (4.47 ± 0.30 mg L^{-1}) were introduced in the reaction vessel under magnetic stirring at 60 min. **Table 1** presents the experimental conditions for each applied treatment.

Table 1. Experimental conditions applied for TC degradation.

Treatment	$[H_2O_2]$	$[Fe^{+2}]$
Solar	None	none
Solar/H_2O_2	0.9^b	none
Solar/H_2O_2	2.6^b	none
Solar-Fenton	2.6^b	378^a
Fenton (dark)	2.6^b	378^a

^{a} mg L^{-1}, ^{b} mol L^{-1}.

Results and Discussion

Table 2 presents the physicochemical characterization in this study adhered to the Standard Methods for the Examination of Water and Wastewater [8]. **Table 3** presents the effect of the Solar Fenton-based process on TC degradation in the sludge matrix.

Table 2. Physicochemical parameters of Barueri MWWTP.

pH	DO* (mg O_2 L^{-1})	Conductivity (µS cm^{-1})	COD** (mg L^{-1})	Alkalinity (mg L^{-1})
6.87 ± 0.5	6.87 ± 0.5	6.87 ± 0.5	6.87 ± 0.5	6.87 ± 0.5

DO*: dissolved oxygen, COD**: Chemical Oxygen Demand

Table 3. Removal efficiency (%), k_{obs}, and R^2 were obtained for solar-driven treatments in synthetic solutions. $[TC]_0$ = 4.47 ± 0.30 mg L^{-1}. Runs performed in duplicate.

Treatment	Removal (%)	k_{obs} (min^{-1})	R^2
Solar	3.4 ± 0.3	0.006	0.7219
Solar/H_2O_2	58.3 ± 0.1	0.0934	0.9506
Fenton	33.7 ± 1.5	0.0180	0.8620
Solar-Fenton	66.6 ± 1.7	0.1679	0.9200

TC degradation efficiency ranking order was set up as Solar-Fenton > Solar/H_2O_2 > Fenton > Solar, according to **Table 3**. Han *et al.* [9] evaluated the feasibility of the Fento-based process to degrade TC and oxytetracycline (OTC), in synthetic solutions, both in concentrations of 1 to 10 mg L^{-1}. Among the results, Han *et al.* [9] observed that the photo-Fenton process was the most effective way to remove TC and OTC when compared to the H_2O_2, UV, and UV/H_2O_2 processes, as identified in the present study.

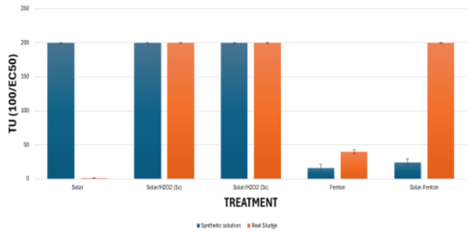

Figure 1. Acute toxicity (in toxic units, TU = 100/EC50) was assessed using *D. similis.* $[TC]_0$ = 4.47 ± 0.30 mg L^{-1}. Runs performed in duplicate. Treatment: 60 min.

Figure 1 shows the acute toxicity of treated matrices, being TC in water and real sludge, previously the process classified as nontoxic (EC50<0.5). Regarding ecotoxic evaluation the process which proved toxic by-products formation was Fenton for synthetic and real sludge, whereas TC synthetic solution was also classified as toxic after the Solar-Fenton process. Han *et al.* [9] estimated the ecotoxicity of TC and OTC by-products with ECOSAR, which indicated that identified photo transformation through photo-Fenton was not toxic for *Daphnia magna* as to *Vibrio Fischeri* and *Green algae.*

Conclusions

Based on the main findings it can be concluded that treatment via Solar-Fenton showed the best efficiency in removing TC, however, toxic by-products were formed in the synthetic solution, suggesting that a longer treatment interval should be adopted.

Acknowledgments

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