Degradation of tetracycline in water by the ultraviolet/sodium percarbonate (UVC/SPC) process

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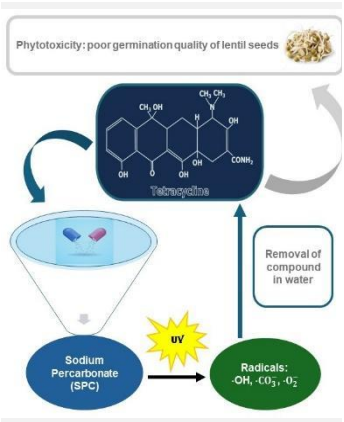

The antibiotic tetracycline (TC) is commonly found in various water sources, posing a serious threat to the health of aquatic organisms. The ultraviolet/sodium percarbonate (UVC/SPC) process has been proposed to improve the removal of TC from wastewater. This study examined the degradation of TC under different UVC and UVC/SPC conditions with the same initial TC concentration (5 mg L^{-1}) for a total volume of 4.5 L. The results indicated that the UVC/SPC system was effective in eliminating TC, with 94.6% of TC removal and a pseudo-first-order specific degradation rate of 2.909 min^{-1} in two minutes, higher than that obtained by direct photolysis, for an initial concentration of $[SPC]_0$ = 93.6 mg L^{-1} and UVC radiant power of 15.6 W. Phytotoxic effects were observed for untreated TC solutions, with the UVC/SPC treatment clearly contributing to the reduction in the toxic nature of TC solutions under the optimum conditions evaluated. In summary, the results suggest that SPC can potentially replace aqueous hydrogen peroxide (H_2O_2) in wastewater treatment.

Introduction

Tetracyclines are broad-spectrum polypeptide antibiotics that inhibit the growth of various bacteria, both aerobic and anaerobic [1]. They may threaten humans and nature due to their role in antibiotic resistance and toxicity [2]. Conventional treatment systems are ineffective in removing these contaminants due to the stability of tetracycline. The UVC/SPC process uses ultraviolet light to activate H_2O_2 and generate mainly hydroxyl radicals that degrade tetracycline (Eqs. 1-7) [3]:

$$Na_2CO_3 \cdot 1.5\ H_2O_2 \rightarrow Na_2CO_3 + 1.5\ H_2O_2 \quad (1)$$

$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \quad (2)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2{}^{\bullet} \quad (3)$$

$$HO_2{}^{\bullet} \rightarrow H^+ + {}^{\bullet}O_2^- \quad (4)$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow {}^{\bullet}CO_3^- + OH^- \quad (5)$$

$$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O \quad (6)$$

$$HCO_4^- + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}CO_3^- \quad (7)$$

This study aims to evaluate the effectiveness of the UVC/SPC process in eliminating tetracycline, considering the effects of initial SPC dosage and UVC radiation dose.

Material and methods

Reagents: each solution was prepared in ultrapure water (Millipore Milli-Q®). Tetracycline (T3258, 98-102%, $C_{22}H_{24}N_2O_8$) and sodium percarbonate (SPC, $Na_2CO_3.1.5H_2O_2$, 20-30% H_2O_2) supplied by Sigma Aldrich were used in the experiments. For HPLC analysis, methanol (HPLC grade), acetonitrile (HPLC grade), and formic acid (CH_2O_2, 98-100%), obtained from Lab Synth, were used. All other chemicals were of analytical grade: H_2SO_4 0.01 mol L^{-1} and NaOH 0.1 mol L^{-1}, obtained from Sigma Aldrich.

***UVC and UVC/SPC processes*:** The photolysis and photo-oxidative degradation experiments were carried out in a photochemical reactor consisting of a borosilicate glass tube containing a concentric low-pressure mercury vapor lamp [6]. The assays were carried out in duplicate using UVC light for a total of 60 minutes. The pH of the TC solutions was monitored with a pH meter (Tecnal, Tec-3MP). Table 1 shows the conditions applied in each experiment.

Table 1. Experimental conditions for TC photolytic and photocatalytic degradation.

Treatment	SPC (mg L^{-1})	UVC radiant power (W)
Photolysis 1	-	3.0
Photolysis 2	-	15.6
UVC/SPC 1	62.4	3.0
UVC/SPC 2	93.6	3.0
UVC/SPC 3	124.8	3.0
UVC/SPC 4	93.6	15.6

Phytotoxicity: sterilized plastic Petri dishes and filter paper were used to place lentil seeds (mixed class, Type 1). The test was carried out in duplicate, using 4 mL of each treated and untreated TC solution; the positive control (PC) was ultrapure water, and the negative control (NC) was $ZnSO_4$ (6 g L^{-1}). The total germination time was 5 days. The germination index (GI) was calculated using Eq. 8, NSG is the number of germinated seeds (≥ 5 cm), NST is the total number of seeds [7].

IG = (NSG/NST) * 100 (8)

HPLC: High-performance liquid chromatography was carried out using Shimadzu equipment (LC-6AD) with a UV-visible detector (SPD-M20A) and a C18 column (250 mm, 4.6 mm, 4 µm). Dilution of stock solutions generated calibration curves to obtain TC standards ranging from 0.5 to 50.0 mg L^{-1}. An isocratic method was applied using a mixture of 15% acetonitrile and 85% formic acid (1%, v/v) [8], and a flow rate of 1 mL min^{-1}. The injection volume, column temperature and analysis wavelength were 100 µL, 35 °C and 276 nm, respectively.

Results and discussion

Figure 1 shows the removal of TC when its detection was possible (LOQ = 0.12 mg L^{-1} and LOD = 0.04 mg L^{-1}).

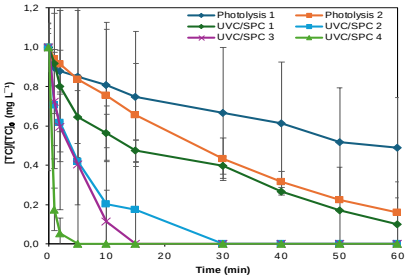

Figure 1. Photodegradation of TC as a function of time in the photolysis and UVC/SPC processes (duplicate experiments) ($[TC]_0$ = 5.74 ± 0.4 mg L^{-1}).

The results showed that a decrease in UVC power has the greatest influence on TC removal. The greatest removal is achieved in the UVC/SPC 4 process, with 94.6 ± 0.1% removal and k_{obs} 2.909 min^{-1} in only 2 min; the initial pH of the TC solution without the addition of SPC was approximately 7.4 ± 0.1, and the maximum value identified after the addition of SPC was approximately 10.5 ± 0.1. In the case of photolysis treatments, there was no significant variation in pH. In the photolysis 2 treatment, 83.8 ± 0.0% removal and k_{obs} 1.818 min^{-1} were obtained after 60 min. In a study conducted by Kyere-Yeboah and Qiao (2023) on the degradation of TC and OTC by non-thermal plasma-activated SPC, the addition of SPC to the antibiotic solution resulted in an increase in alkalinity of the solution from 5.8 (in the absence of SPC) to 9.2. It was shown that the alkalinity of the solution was beneficial for the release of H_2O_2 molecules from SPC, which further contributed to the generation of hydroxyl radicals, an indispensable factor in the degradation of antibiotics. As the pH increases, the proportion of the anionic form of TC progressively increases. In the investigation by Zhao *et al.* (2024), it was found that the anionic form of TC was less stable and more susceptible to photooxidation, additionally, the $CO_3^{\bullet-}$ radicals generated at high pH also influenced the degradation of TC.

The phytotoxicity tests with lentil seeds revealed the detrimental effects of TC on plant growth. The highest germination index (83 ± 0.1%) was observed when the percentage of TC removal was higher (Fig. 2), indicating the direct correlation between TC removal and the health of the plant seeds. In this case, the samples collected for phytotoxicity analysis after 10 minutes of treatment showed a germination rate of 99.0%.

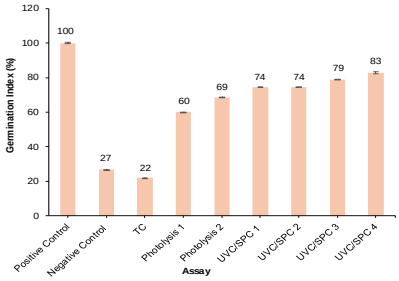

Figure 2. Germination index of lentil seeds exposed for 5 days to ultrapure water (positive control), $ZnSO_4$ (negative control), untreated tetracycline solution and tetracycline solutions treated by photolysis and UVC/SPC (duplicate tests) ($[TC]_0$ = 5.74 ± 0.4 mg L^{-1}).

Conclusions

The UVC/SPC process proved effective for the degradation of tetracycline in aqueous medium, with 94.6 ± 0.1% removal in only two minutes and a pseudo-first specific degradation rate of 2.909 min^{-1} under the best conditions studied. Phytotoxic effects were observed for untreated TC solutions, with the UVC/PS treatment clearly contributing to the reduction in the toxic nature of TC solutions under the optimum conditions evaluated. Compared to conventional UVC/H_2O_2, the UVC/SPC process has a clear cost-benefit in terms of process safety and reduced freight and storage costs, due to the lower cost and ease of handling of the solid source of hydrogen peroxide. In this context, sodium percarbonate (SPC) can potentially replace aqueous hydrogen peroxide (H_2O_2) in wastewater treatment.

Acknowledgments

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