Tetracycline degradation through hydrodynamic cavitation: operating conditions and phytotoxic investigation with *Lens culinaris*

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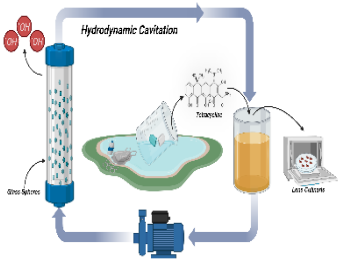

The work addresses the degradation of tetracycline (TC), a widely used antibiotic and potential environmental contaminant, by hydrodynamic cavitation using a fixed-bed reactor filled with glass beads. An initial concentration of 10 mg L^{-1} of TC was used, with 3 liters as the total volume. The kinetics was investigated at different degradation times, obtaining a linear decay of concentration over time and 88.7% TC removal by means of the process operated with a fixed bed of glass beads and 91.9% without beads. The test carried out using lentil (*Lens culinaris*) seeds, based on the germination index, confirmed that the treated water showed phytotoxicity effects.

Introduction

Water is exposed employing contamination [1]. A very important group of emerging contaminants (ECs) are pharmaceuticals, and their presence in drinking water has generated concerns associated with the threat they pose [2]. Conventional water treatments have not been very effective in removing these contaminants [1].

Over the years, it has been shown that the techniques for removing or eliminating antibiotics present in wastewater are [3]: adsorption, biodegradation, and advanced oxidation [4]. Advanced chemical oxidation processes use oxidants to reduce biological oxygen demand (BOD) and high chemical oxygen demand (COD) [5]. Hydrodynamic cavitation (HC) occurs when the dynamic pressure of a liquid is reduced by constriction devices such as Venturi, orifice plates, etc. [6]. The cavities are driven into a higher-pressure region and implode, causing very high local pressures and temperatures. The rupture of the cavitation bubbles also usually initiates some physicochemical effects, such as shock waves, the formation of reactive radicals, and the production of shear forces [7].

This study focuses on the application of an HC device, which is used for the degradation of tetracycline, by means of a reactor with and without a bed of glass beads. In addition, hydrolysis was investigated varying pH (natural, acid and alkaline) and a phytotoxicity test was carried out using lentil (*Lens culinaris*) seeds.

Material and Methods

Tetracycline (98-102%, $C_{22}H_{24}N_2O_8$) was supplied by Sigma-Aldrich. Methanol (HPLC grade) and formic acid 85% (Lab Synth) were used to prepare the mobile phases used in liquid chromatography. The solutions were prepared using the water 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. The chemicals were used as supplied and without any additional purification.

Hydrodynamic Cavitation. The tetracycline degradation tests were carried out in a closed-loop treatment system comprising a water tank, a cavitation reactor (vertical cylindrical column with a total height of 60 cm and an internal diameter of 6 cm), a high-pressure pump (BC-92S 1C 2 T 60 2/3), a pressure gauge and two control valves. All the experiments were carried out using a total volume of 3 L and a TC concentration of 10 mg L^{-1}. The reactor was filled with 12.8-mm diameter glass beads.

HPLC. High-resolution liquid chromatography was performed using a Shimadzu (LC-6AD) equipment equipped with a UV-visible detector (SPD-M20A) and C18 column (250 mm, 4.6 mm, 4 µm). 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. The calibration curves were obtained by diluting the stock solutions to obtain the TC standards from 0.5-50.0 mg L^{-1}.

Phytotoxic assay. The phytotoxicity tests were carried out with lentil (*Lens culinaris*) seeds. The experiments were carried out in duplicate, using 10 seeds per Petri dish, with 4 mL of sample. For the germination of the lentils, a refrigerated incubator with agitation (TE-421) was used, kept at 20°C and absolute darkness for 5 days.

Germination Index

$$(IG) = \frac{NSG}{NST} * 100 \quad (1)$$

Root Growth Rate

$$(IC) = \frac{CA}{CC} * 100 \quad (2)$$

Where: NSG: Number of germinated seeds (≥ 5 cm);

NST: Number of total seeds; CA: Sample length (cm); CC: Length of the negative control (Milli-Q water) (cm).

Results and Discussion

The results obtained are shown in **Table 1**. The presence of glass beads did not significantly alter the % removal of TC and the removal rate.

Table 1. Removal efficiency (%), $k_{obs,}$ and R^2 were obtained for hydrodynamic cavitation treatments. $[TC]_0$ = 10 mg L^{-1}. Runs performed in duplicate.

Treatments	Removal (%)	k_{obs} (min^{-1})	R^2
HC with glass beads	**88.7 ± 0.6**	**0.0726**	**0.92**
HC without beads	**91.9 ± 0.3**	**0.0881**	**0.89**

According to the results shown in Figure 1, the solutions treated in the presence of glass beads (HC-B) resulted in a 3.8-fold reduction in *L. culinaris* root growth compared to HC alone. In addition, HC-B also provided a 2.1-fold reduction compared to TC the solution. These results suggest a distinct degradation pathway depending on the configuration of the HC reactor.

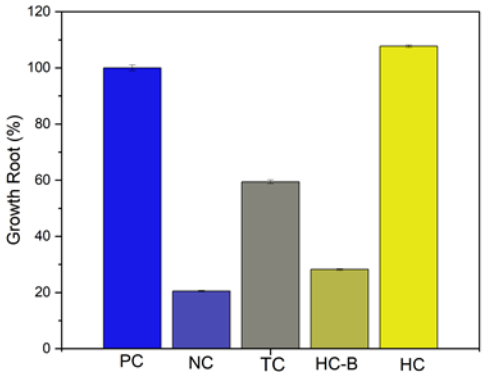

Figure 1. Results of the phytotoxicity tests with *L. culinaris* seeds. PC = positive control (Milli-Q water); NC = negative control ($ZnSO_4$,150 mg L^{-1}); TC = tetracycline solution (TC, 10 mg L^{-1}); HC-B = hydrodynamic cavitation in the presence of glass beads; HC = hydrodynamic cavitation without beads.

Mohod et al. [9] evaluated the effect of HC on Rhodamine 6G (Rh 6G) and the phytotoxic to *L. culinaris*. The Rh 6G solution treated in an air-beads cavitation column for 180 min (2 mL L^{-1} of H_2O_2) promoted a delay in cell division and genotoxic effects, also suggesting phytotoxic effects, as observed in the present study.

Conclusions

The fixed bed cavitation system demonstrates high-efficiency TC degradation, with and without glass beads, reaching removals of 88.7% and 91.9% in 35 min, respectively. After 120 hours of germination of *Lens Culinaris* seeds, phytotoxic effects were observed for treated and untreated solutions, suggesting the generation of hazardous by-products after the HC with glass beads.

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