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Highly-efficient tetracycline degradation under simultaneous hydrodynamic cavitation and electrical discharge plasma in flow

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Abstract

Tetracyclines are widely used antibiotics that are often carelessly released into the environment, posing a potential threat to the ecosystem. Due to the lack of efficient methods to remove tetracyclines from wastewater, a remarkable research effort on the remediation of tetracyclines has been undertaken. The synergistic effect of hydrodynamic cavitation (HC) and electrical discharge (ED) plasma on the degradation of a number of antibiotics in water has been studied in this work. Catalyst- and oxidant-free processes have been carried out using a new pilot-scale hybrid device (HC/ED plasma) working in flow-through mode (330 L/h). Tetracycline hydrochloride (TC), doxycycline hyclate (DC) and oxytetracycline dihydrate (OC) were selected as the model compounds. Antibiotic degradation tests were performed using a 5-litre water solution at various antibiotic concentrations (10, 25, 50, 75, and 100 mg/L). All experiments were performed over 15 minutes, and samples were either collected using the flow-through method, or every 5 minutes when using the loop configuration. The temperature was kept constant at 30°C, with fluctuations of $\pm 2^\circ\text{C}$. The influence of applied HC input pressure (45, 60 and 70 bar), applied ED amplitude frequency (10 and 48 kHz) and the pH values of the initial solutions (2 and 11) on antibiotic-degradation rate have been investigated. Near quantitative TC (> 98%), DC (98%) and OC (95%) degradation was documented after only 15 min of combined HC/ED plasma treatment at 70 bar and 48 kHz. To better understand the synergistic effect of coupled HC/ED treatment on antibiotic degradation, a dosimetry assay was performed to quantify the oxidizing compounds generated by this technology. Specifically, the coupled HC/ED plasma treatment was able to linearly increase the amount of oxidants in water as a function of time, reaching a maximum concentration of 13.426 mmol/L after 15 minutes, which is more than 85-times higher than that of HC alone (0.153 mmol/L). This study demonstrates the impressive efficiency of hybrid HC/ED plasma technology in degrading recalcitrant antibiotics in wastewater without the need for catalysts and oxidants.

1. Introduction

In recent years, pharmaceuticals have been defined as “new emerging pollutants” in aqueous environments, with antibiotics being one of the most widespread due to their extensive use in the treatment of human and animal infections.^{1,2} In particular, antibiotic moieties that are highly water-soluble and poorly biodegradable have been detected in many aquatic systems in recent decades, resulting in serious threat to both public health and the natural environment, not only because of their toxicity, but also because bacteria have become resistant to certain antibiotics as a result of their heavy use.^{3,4} Tetracyclines (TC) are the second most used and produced antibiotics due to their low price and broad-spectrum of bactericidal action.⁵ Nevertheless, TCs are not completely absorbed in the body and have poor metabolic degradation, meaning that they are discharged into the environment via urine and feces. Moreover, tetracyclines are chemically stable and not easily degradable, making them difficult to remove from the environment.⁶⁻⁸ Suitable processes to effectively degrade antibiotics in wastewater must therefore be developed. Besides adsorption,⁹ nanofiltration¹⁰ and hydrothermal treatment¹¹,

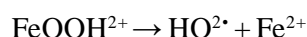
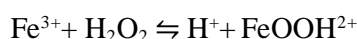
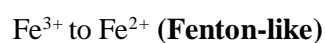
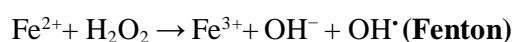
advanced oxidation processes (AOPs)¹²⁻¹⁴ are the most commonly employed and cost-effective technologies for the complete degradation of persistent organic contaminants, such as TC and other antibiotics, in wastewater.¹⁵ AOPs have recently been successfully coupled with several emerging technologies, such as cavitation treatment¹⁶ and non-thermal plasma technologies,^{17,18} in order to enhance their ability to degrade antibiotics via OH-radical production.

The main individual AOP techniques can be categorized by technology and oxidant.

The different technologies are: photocatalysis, ultrasound, microwaves, electro-chemical oxidation and wet oxidation.¹⁹ Each of these can either be used alone or in association with another technology (hybrid). The combination of two or more individual AOPs (hybrid AOP) can considerably improve the efficiency of organic-compound degradation.²⁰ For example, the three most applied AOP techniques are O₃/H₂O₂, H₂O₂/UV and O₃/UV.²¹

The most used oxidants are Fenton, Fenton-like, O₃ and H₂O₂.

The addition of H₂O₂ to Fe²⁺ salts generates OH-radical production via the Fenton reagent.



The Fenton reagent reacts at pH 2–3 and produces a large quantity of iron sludge, which causes treatment problems,²² whereas the use of O₃ can lead to respiratory-system diseases.²³

In the field of wastewater treatment, hydrodynamic Cavitation (HC) help to overcome the mass transfer limits of most advanced oxidation processes (AOP) that are not able to completely degrade complex compounds, while also reducing oxidant consumption and process costs, and increasing energy efficiency.

HC is considered a promising technology and has been widely applied in many fields, such as food processing,²⁴ the removal of pharmaceuticals and biological organisms (bacteria, cyan bacteria and viruses),²⁵ and biodiesel synthesis.²⁶

HC is one of four ways to create cavitation phenomena, together with acoustic cavitation (AC), optic cavitation (OC) and particle cavitation (PC).²⁷

Cavitation is defined as the nucleation, growth and implosion of cavitation bubbles in a very short time s, as caused either by the passage of ultrasound, or by alterations in flow and pressure. The result is high temperatures, high pressures and high jet flows.²⁸

Under cavitation conditions, water molecules can decompose into different oxidants, including ·OH, ·OOH, H₂O₂, etc., which can react with pollutants in wastewater, while the implosion forces that are generated when cavitation bubbles collapse can destroy the molecular bonds of organic pollutants and make them thermally decompose.

Cavitation phenomena are generated by pressure and flow variations in the liquids that are induced by geometric constrictions, such as orifice plates, venturi and nozzles, which are equivalents to a throttle valve.²⁹ According to Bernoulli's equation, when a fluid flows through a reduction in the cross-section of the channel, the kinetic energy increases and the pressure decreases. If the pressure drops to the saturated vapor pressure at the operating temperature, bubbles begin to form and grow, and the size of cavitation bubbles can vary from a few nanometers to a few millimeters depending on flow conditions. Once the pressure rises above the vapor pressure, the bubbles collapse and the micro-jets generate turbulence downstream of the constriction.³⁰

There are four types of HC reactor: venturi type reactors; orifice type reactors; rotating type reactors; and vortex rotating type reactors. Of these different technologies, venturi and orifice plates are most widely used as cavitating devices in HC reactors thanks to their simplicity, ease of use and low maintenance costs. While there are currently several studies that focus on the reactor types and parameters that can increase degradation efficiency, there are also many studies that have demonstrated the high efficiency and sustainability of hybrid technologies that combine HC and other AOPs.^{31,32}

Non-thermal plasma (NTP) technology is one such emerging advanced oxidation method and has recently been used in combination with HC to treat various pollutants, receiving widespread attention thanks to the advantages that it offers, which include high efficiency, simplicity and an environmentally-friendly approach.¹⁸

However, developing more effective and safe non-thermal plasma technologies for use in pollutant-treatment applications is still a challenge, and this is especially true for the development of efficient application-based instruments. In this work, we therefore present a novel approach to the application of ED plasma in the processing of tetracyclines in combination with a pilot HC device. The degradation efficiency of tetracyclines (TC, DC, OC) in aqueous solution, using new laboratory hybrid equipment that simultaneously combines HC and ED plasma, has been determined. The effects of the reactor inlet pressure, pH value and initial concentration on tetracycline degradation have been evaluated.

2. Materials and methods

2.1 Chemicals

Tetracycline hydrochloride (>96%) and doxycycline hyclate were purchased from Alfa Aesar. Oxytetracycline dihydrate (>98%) was purchased from Sigma Aldrich. All solutions were prepared by dissolving the antibiotic in distilled purified water and tap water.

2.2 General pilot-scale HC/ED experimental set up and cycline-degradation procedure

A schematic diagram of the experimental setup is shown in Figure 1 a. The combined reactor is equipped with a 30 L tank for contaminated water, a triplex plunger high-pressure pump (3.3 kW power, SPECK Pumpen Verkaufsgesellschaft GmbH, Neunkirchen am Sand, Germany), a quartz cylinder discharge chamber (length-200 mm, diameter-8 mm) (Figure 1b) with two brass electrodes (4 mm thickness), and a HC unit (Figure 2a), which included a fitting for the high pressure line and a 4-holed (4 mm for each hole) orifice plate (Figure 2b). Further orifice-plate-hole restrictions (2 mm) are generated once the HC unit is assembled (Figure 2c). An alternating voltage of 15 kV is applied to the two electrodes to generate the ED plasma. The electrical discharge power (0 to 5 kW) and its amplitude frequency (10 kHz or 48 kHz) are regulated from the control panel. The inlet pressure (40 to 70 bars) is regulated by the pressure regulator of the pump. The temperature of the contaminated water was kept constant using a chiller unit (H150-1000, LabTech, Italy) linked to a coil heat exchanger placed inside tank. The cavitation number (C_v) of the system was calculated in a previous work and was approximated to 0.0027 for this work³³. Moreover, additional details on how works the exploited hybrid pilot scale reactor are reported in Figure S1 and S2 for the HC-alone mode configuration (ED off), and in Figure S3, S4 for the combined HC/ED mode. The pilot scale hybrid HC/ED reactor adopted in this work exploits the electrical discharge in bubbles/vapor technology. Due to this reason, discharge induces the plasma generation inside cavitation bubbles only if they are generated. ED plasma follows the “cavitation front” only when the inlet pressure is high enough to induce cavitation (Figure S3 and Figure S4). Beyond the “cavitation front” the discharge is not capable to induce the generation of plasma in water because of the intrinsic nature of the reactor.

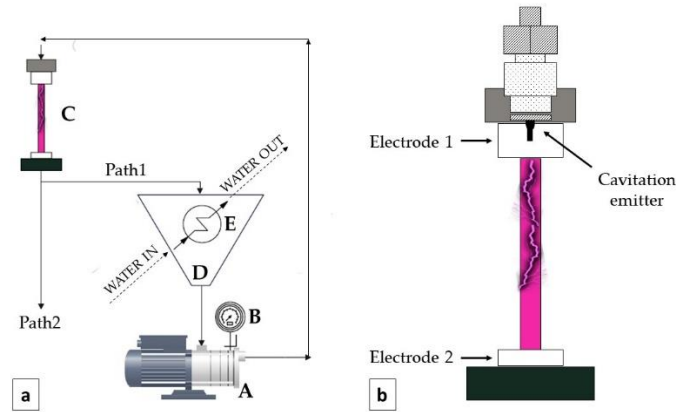


Figure 1. a) Scheme of the **pilot scale** hybrid reactor set-up. A: Pump; B: Manometer; C: Reaction chamber; D: Reservoir tank; E: Heat exchanger. Path1 : Loop configuration; Path 2: Flow configuration. B) Detail of the reaction chamber.

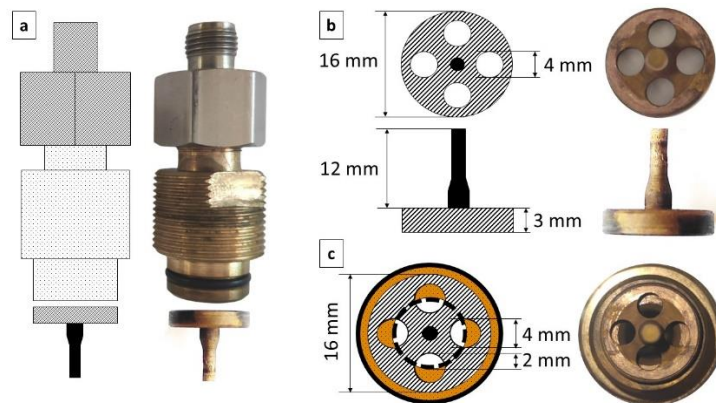


Figure 2. a) HC unit. B) Details of the orifice plate. C) Orifice-plate-hole restrictions.

The degradation of three different types of tetracyclines was investigated: tetracycline hydrochloride (TC); doxycycline hyclate (DC); and oxytetracycline dihydrate (OC). The degradation tests were performed using a total contaminated-water volume of 5 L at different applied pressures (45, 60 and 70 bars) and at different starting antibiotic concentrations (10, 25, 50, 75 and 100 mg/L). All experiments were carried out for a total time of 15 minutes and the samples were either collected in flow configuration or every 5 minutes in loop configuration. The temperature was kept constant at 30°C with fluctuations of $\pm 2^\circ\text{C}$. The effect of pH values (2 and 11) was also investigated.

2.3 General “lab-scale HC” experimental set up and procedure for tetracycline degradation

The lab-scale HC device consists of a 1.1 kW centrifugal pump (Speck GY-028-2, 2750 rpm, Roth, Germany), a suction orifice plate (thickness 1 mm, inner diameter 5 mm) and a suction Venturi tube (inner diameter 5 mm), a coil heat exchanger, a water tank (800 mL) and a manometer for the measurement of the suction pressure (0.75 bar). The cavitation number (C_v) value is 0.2.³⁴ 800 mL of a 50 mg/L solution of TC was recirculated inside the HC unit for a total time of 15 minutes. The temperature was kept constant at 30°C, with fluctuations of $\pm 2^\circ\text{C}$, via the recirculation of tap water inside the heat exchanger. Samples were collected every 5 minutes of treatment.

2.4 General procedure for tetracycline-degradation-rate analyses in relation to cavitation parameters

The concentrations of all the treated samples were measured using a UV-vis spectrophotometer (Agilent Cary 60 UV-Vis) at a wavelength specific for the three antibiotics (TC – 355 nm; DC and OC – 375 nm), and in function of the maximum absorbance observed at pH 2 and 11 (Figure S5, S6 and S7). The degradation rate was calculated according to equation 1:

$$\text{Degradation Rate} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where C_0 is the concentration of the solution to be subjected to treatment and C_t is the concentration of the sample taken at the beginning or at any other time. The concentrations of the tetracyclines were evaluated using a UV spectrophotometer at a specific wavelength for each type of TC, specifically 355 nm for tetracycline and 374 nm for DC and OC.

The cavitation number was used to characterize the cavitation conditions of all of the degradation experiments. It is a dimensionless number calculated using equation 2:

$$C_v = \frac{P_2 - P_v}{\left(\frac{1}{2}\right)\rho v_0^2} \quad (2)$$

Where P_2 is the pressure downstream of the constriction (Pa), P_v is the vapor pressure of the fluid (Pa), ρ is the density of the fluid (kg/m^3) and v_0 is the liquid velocity at the throat of the constriction. Typically, under ideal conditions, cavitation phenomena occur if $C_v \leq 1$. When the cavitation number is low, the number of cavities is high, and the intensity of cavitation is also high. It is possible to increase the cavitation intensity by controlling the pressure in the region where cavities collapse.²⁹

The cavitation yield was calculated using equation 3:

$$\text{Cavitation Yield} = \frac{\text{amount of pollutant degraded}}{P_m t} \times 100\% \quad (3)$$

Where P_m is the power of the pump (W) and t is the operation time (s).

3. Results and discussion

3.1 HC- vs HC/ED-assisted tetracycline degradation

The synergistic effect of hydrodynamic cavitation (HC) and electrical discharge (ED) plasma was first investigated for TC degradation in water in the new pilot-scale hybrid device working at 330 L/h (Figures 1 and 2). The TC degradation tests were performed on a 5 L water solution with different antibiotic concentrations (10, 25, 50, 75 and 100 mg/L). All experiments were carried out for a total time of 15 minutes and the samples were either collected in flow configuration or every 5 minutes in loop configuration. The temperature was kept constant at 30°C with fluctuations of $\pm 2^\circ\text{C}$. The effects of applied pressure (45, 60 and 70 bars) and pH values (2 and 11) were investigated. In particular, in order to investigate the effectiveness of the *in-situ* generated ED plasma at increasing TC degradation under HC/ED treatment (pilot-scale), compared to treatments performed under HC alone, three different degradation tests were first performed at a fixed inlet pressure of 70 bar and an initial TC concentration of 50 mg/L. The same pilot scale reactor described in Figure 1 was exploited either with the ED plasma “on” (hybrid HC/ED plasma treatment with a frequency discharge of either 10 kHz or 48 kHz) or “off” (HC pilot-scale treatment) (Figure 3a). During the degradation test performed with HC alone, a degradation rate of 36.4% was observed in the flow configuration, while a maximum degradation of 50.0% was observed after 15 minutes of treatment in the loop configuration.

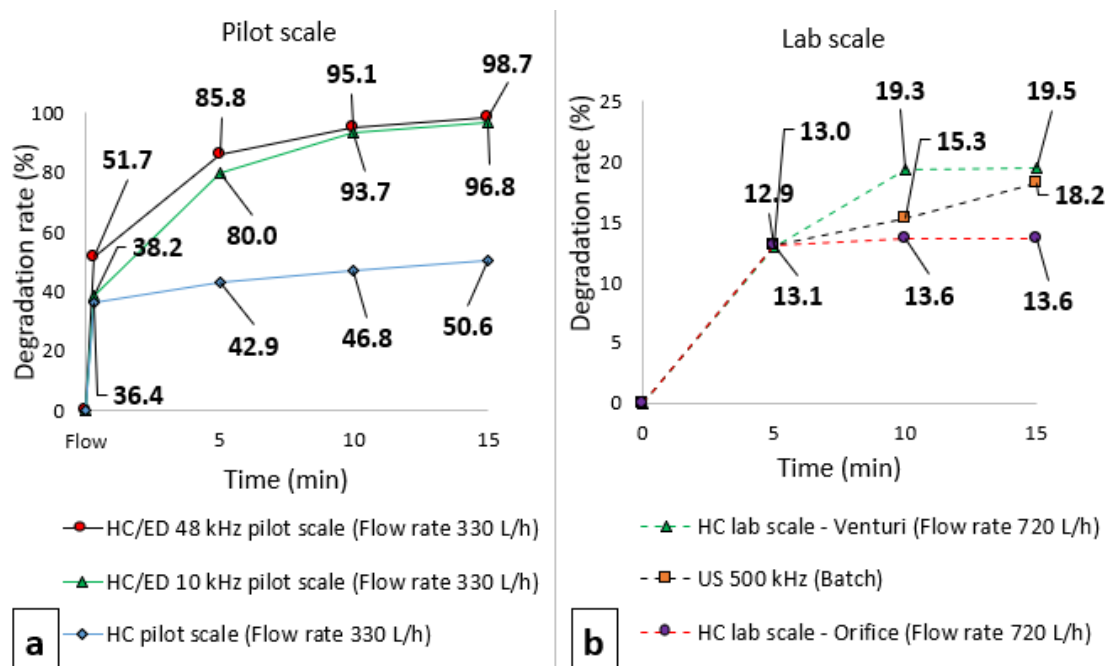


Figure 3. Comparison between pilot scale and lab scale cavitation devices a) Influence of ED frequency on TC degradation (C_0 :50 mg/L): pilot scale HC vs pilot scale HC coupled with ED in (tap)water. b) TC degradation: HC lab scale (orifice & venturi mode) and US (500 kHz) in (tap)water.

For the sake of comparison, further cavitation treatments were performed on the same TC solution (50 mg/L) in a lab-scale HC unit and in an ultrasonic bath. In detail, the lab-scale HC treatment was performed using an orifice plate of 5 mm diameter (resultant vacuum of -0.75 bar) and a venturi tube of 5 mm (resultant vacuum of -0.4 bar), while the US treatment was conducted on 100 mL of a 50 mg/L TC solution in a ultrasonic bath, equipped with 3 piezo actuators, connected to a ultrasonic generator (UMC250TD500, WeberUltrasonics AG, Karlsbad, Germany) with an output frequency of 500 kHz and power of 200 W. As shown in Figure 3b, the lowest degradation rate after 15 min (13.6%) was obtained with HC performed with an orifice plate set-up (thickness 1 mm, inner diameter 5 mm), while this slightly increased to 19.5% using the venturi tube (inner diameter 5 mm). US treatment provided a TC-degradation value of 18.2%, which is similar to the one observed at the end of the venturi-HC treatment.

TC degradation under HC alone has previously been reported as being carried out in different HC units and using different oxidation strategies (Table 1). For example, Jun Qin *et al.*,³⁵ observed a degradation of 20.0% after 15 minutes of HC treatment when the inlet HC pressure adopted was 3 bar and the starting TC concentration was 5 mg/L (total volume of 5 L). Wang *et al.*,³⁶ were able to degrade TC by 12.2% after 90 minutes with an inlet pressure of 2 bar and a starting antibiotic concentration of 30 mg/L (total volume of 2 L).

In general, both HC/ED treatments in our work (10 kHz and 48 kHz) conducted in pilot scale led to an increase in TC degradation (Figure 3a). Specifically, the maximum degradation rate was 96.8% at an applied frequency of 10 kHz after 15 minutes, whilst a frequency of 48 kHz gave 98.7% degradation. Although no substantial differences in degradation rate were observed at the different applied frequencies in loop configuration, a significant difference was observed in flow mode. In fact, a degradation of 38.2% was obtained at 10 kHz, which is similar to the value observed with flow-mode HC alone (36.4%), while it was 51.7% with 48 kHz, confirming that 48 kHz was the best frequency to be applied for HC/ED treatment. A typical Fenton process on a total volume of 250 mL has previously been performed by Gurtekin *et al.*,³⁷ on a 100 mg/L solution of TC in a 250 mL flask under magnetic stirring. The authors observed the complete degradation of the antibiotic after 10 minutes of reaction (performed at pH 4), and 15 additional minutes of sedimentation, using two solutions of Fe²⁺ and H₂O₂ at concentrations of 30 mg/L and 100 mg/L, respectively. A Fenton-like process has been performed by Nie *et al.*,³⁸ using Fe₃O₄ nanospheres for H₂O₂ activation in batch experiments, and a TC degradation of 82% was achieved after 110 minutes of reaction with a catalyst loading of 0.5 g/L, initial TC concentration of 25 mg/L (total volume of 30 mL) and a 50 mM solution of H₂O₂ at neutral pH. Another Fenton-like catalyst has been exploited by Li *et al.*,³⁹ in a photo-Fenton treatment for the degradation of a 100 mL solution (20 mg/L) of TC. In detail, an Fe-doped porous carbon nitride catalyst (Fe/SCN) was synthesized via a supramolecular self-assembly method and then irradiated with simulated visible light inside the reaction mixture in the presence of H₂O₂ (80 mM solution), granting a maximum TC-degradation rate of 90.3% in 80 minutes of treatment. A combined HC and photocatalysis treatment has been performed by Wang *et al.*,³⁶ who used a high loading of UV-irradiated TiO₂ (100 mg/L) as the catalyst for the degradation of a 30 mg/L TC solution, and obtained a maximum degradation rate of 78.2% after 90 minutes of treatment. Electrical-discharge-generated plasma alone has been exploited by Fang *et al.*,⁴⁰ for the treatment of 200 mL of a 200 mg/L solution of TC. Plasma was generated by the application of 20 kV and an amplitude of 9.22 kHz to a mixture of Air-O₂ that was in contact with the solution, with no propagation in the liquid phase. Treatment with cold plasma allowed the authors to degrade the antibiotics by a value of 81.5% after 20 minutes of treatment. Discharge plasma, used alone and in combination with hydroxylamine to promote OH[•] generation, has also been exploited by Huang *et al.*,⁴¹ to treat 300 mL of TC solution. Maximum degradations of 70.7%, with plasma alone, and 90.0%, with plasma combined with hydroxylamine, were obtained after 18 minutes of treatment.

A comparison with literature data has allowed us to establish that the hybridization of HC and ED plasma:

1. intensifies the degradation process, which reduces treatment time and avoids the use of oxidizing compounds and photo-catalysts
2. allows the ED plasma to propagate through the TC solution
3. removes the need for dangerous gases to generate plasma
4. allows higher volumes and TC concentrations to be treated
5. grants promising results in flow mode.

A hybrid prototype system, based on HC technology coupled with ED, for TC degradation (C₀ 40 mg/L) in the presence of 5 mg/L of catalyst has previously been reported by Abramov *et al.* (Table 1).¹⁸ In detail, the authors conducted the experiment in flow mode only, passing the TC solution 1, 2 or 3 times through the discharge chamber (8.6 kV applied voltage and 43 kHz applied amplitude) with no recirculation. After the first cycle, which represents true flow treatment, TC was degraded by a value of 41%, which is slightly higher than that observed in the flow configuration adopted in this work with an amplitude of 10 kHz (38.2%), but lower than

that observed at an applied amplitude of 48 kHz (51.7%) (Figure 3a). After the third cycle, the authors observed a maximum degradation rate of 67%. In general, a comparison of the data obtained using similar HC/ED equipment by Abramov *et al.*, but under different ED-plasma-generation conditions, showed that the application of 15 kV (rather than 8.6 kV) and an amplitude of 48 kHz (rather than 43 kHz) allowed a higher degradation rate to be achieved, with an increment of 26% being observed under flow treatment.

Table 1 Comparison of TC-degradation processes

TC C ₀ (mg/mL)	Scale	AOP technology	Oxidant	Catalyst	Time (min)	Degradation rate (%)	Ref.
5	5 L (loop)	HC	no	no	15	20	Jun Qin <i>et al.</i> ³⁵
30	2 L (loop)	HC	no	no	90	12.2	Wang <i>et al.</i> ³⁶
100	250 mL (batch)	Fenton	Fenton-like Fe ²⁺ /H ₂ O ₂ (100 mg/L)		10 +15	100	Gurtekin <i>et al.</i> ³⁷
25	30 mL (batch)	Fenton-like	Fenton-like Fe ₃ O ₄ nanospheres/H ₂ O ₂		110	82	Nie <i>et. al.</i> ³⁸
20	100 mL (batch)	Vis-light	Fenton-like Fe/SCN-H ₂ O ₂		80	90.3	Li <i>et al.</i> ³⁹
30		HC -UV	no	TiO ₂	90	78.2	Wang <i>et al.</i> ³⁶
200	200 mL (batch)	ED (20 kV-9.22 kHz)	Air-O ₂	no	20	81.5	Fang <i>et al.</i> ⁴⁰
	300 mL (batch)	ED	NH ₂ OH	no	18	90	Huang <i>et al.</i> ⁴¹
40	N.A	HC/ED	no	CeO ₂	flow	41	Abramov <i>et al.</i> ¹⁸
50	5 L (Flow: 330 L/h)	HC/ED	no	no	flow	51.7	This work
					15	98.7	

3.2 Influence of applied pressure on tetracycline degradation under hybrid HC/ED treatment (tap water vs deionized water).

Pilot-scale HC/ED TC-degradation treatments were carried out at different inlet pressures (45, 60 and 70 bars) to investigate the effect of this parameter on the degradation rate of tetracycline hydrochloride with a starting concentration of 50 mg/L. The screening of the applied pressure was performed first on TC dissolved in tap water (composition reported in Table S1) to simulate the conditions of real wastewater. For the sake of comparison, the degradation tests were also performed on dissolved TC in deionized water. As shown in Figures 4 and 5, the extent of degradation increases with an increase in applied pressure both with deionized and tap water. Generally, an increase of inlet pressure during HC treatment leads to a larger pressure drop and a subsequent enhancement of cavitation-bubble generation,³⁶ which results in a greater number of hydroxy radicals being produced and the higher oxidative degradation of organic compounds. In detail, the highest degradation rate observed during the experiments performed with tap water (98.7%) was obtained after 15 minutes of treatment with an applied pressure of 70 bars, which was then selected as the reference pressure value for all subsequent treatments. On the other hand, the complete degradation of TC was observed after 15 minutes at an applied pressure of 60 bars, rather than 70 bars, during the experiments conducted with deionized water. Moreover, at the end of the treatment performed in deionized water with an inlet pressure of 60 bar, the chemical oxygen demand (COD) of the treated water solution was also monitored (Figure S8) and a COD

reduction of 66% was observed after 15 minutes. A decrease in the extent of degradation was observed beyond 60 bar of inlet pressure during the treatment of TC dissolved in deionized water, and this can be ascribed to the generation of a “cavity cloud” caused by a significant increase in the number of cavities, resulting in reduced cavitation intensity.^{42,43} Furthermore, the decrease in the extent of degradation can be also attributed to the formation of larger cavitation bubbles, which agglomerate without collapsing and therefore do not release energy for the generation of hydroxy radicals (super-cavitation).²⁷ The decrease in cavitation intensity observed beyond 60 bar was also confirmed in the evaluation of the cavitation yield (Figure S9). In fact, the cavitation yield was $8.4 \cdot 10^{-5}$ mg/J at 60 bar, while it was $8.2 \cdot 10^{-5}$ mg/J at 70 bar.

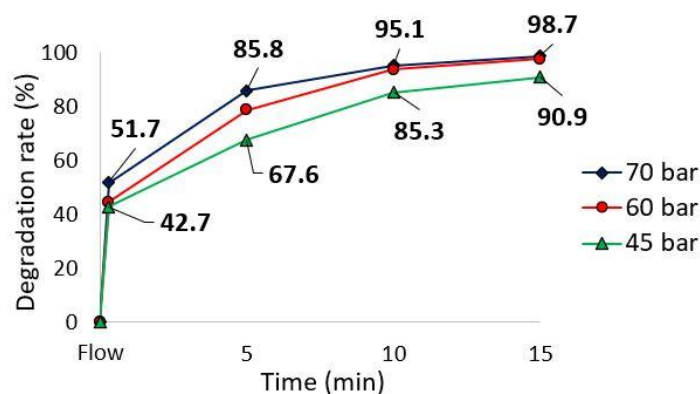


Figure 4. Pilot-scale HC/ED degradation of TC in tap water (influence of pressure).

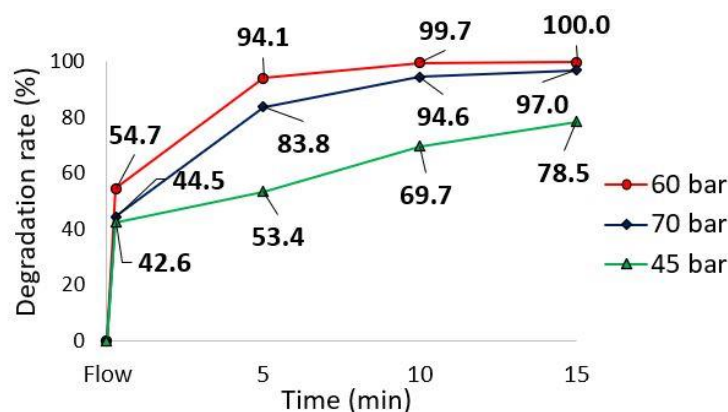


Figure 5. Pilot-scale HC/ED degradation of TC in deionized water (influence of pressure).

In general, the best results were achieved when working at pressures above 50 bar. Specifically, 60 bar of pressure granted the best degradation rate in deionized water (Figure 6), while, in tap water after 10 min of treatment, it was not possible to observe any differences in TC degradation at 60 or 70 bar (Figure 6). Taking these results into account, all further experiments were performed in tap water for convenience and to better fit with real wastewater.

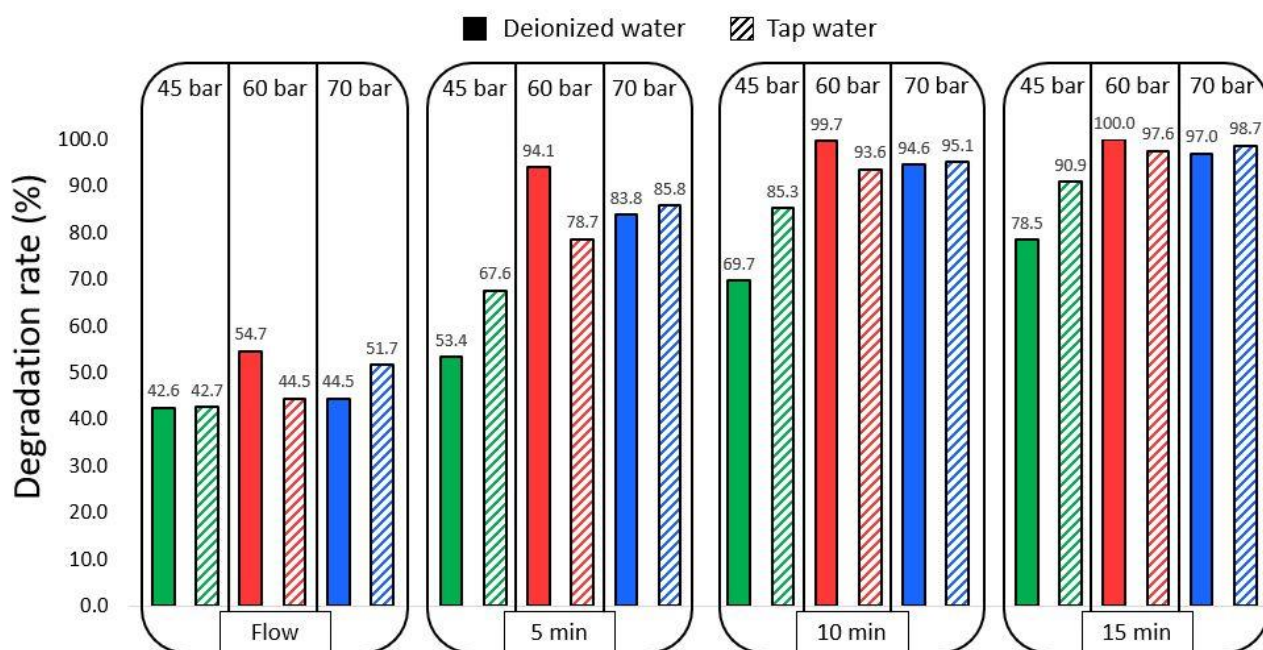


Figure 6. Pilot-scale HC/ED degradation of TC tap water vs deionized water (influence of pressure).

3.3 HC/ED long effect

To better understand the synergistic effect of HC and ED plasma on the degradation of TC, a dosimetry test for the quantification of oxidizing compounds (Weissler Method)⁴⁴ was performed on deionized water treated at 70 bar with HC alone and hybrid HC/ED. As shown in Figure 7, HC alone generated a lower and more constant amount of oxidant compounds than hybrid HC/ED plasma treatment. In detail, after only 1 minute of treatment, HC alone generated 0.131 mmol of oxidants per liter of treated solution, while the hybrid HC/ED technology was able to increase that value to 1.722 mmol of oxidants per liter. In general, ED plasma was capable of linearly increasing the concentration of oxidizing compounds as a function of treatment time, with the maximum concentration of 13.426 mmol/L being reached after 15 minutes.

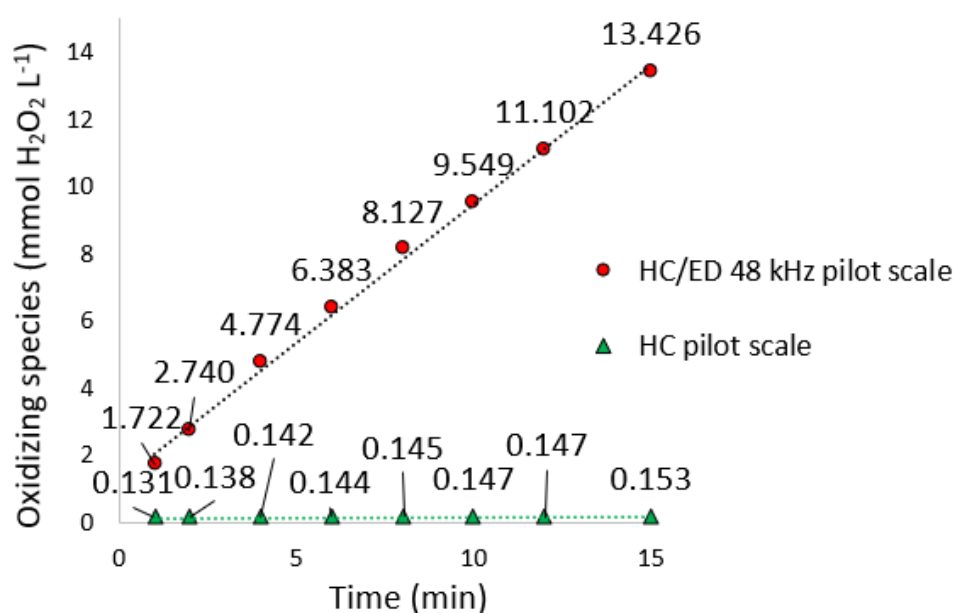


Figure 7. Oxidant dosimetry test in water (Weissler Method)⁴⁴ HC vs hybrid HC/ED plasma.

Seeing as several oxidizing species, such as short-lifetime ROS (hydroxy radicals), stable ROS (H_2O_2), O_3 and UV light, were generated by the propagation of ED plasma through the cavitation bubbles,³³ different TC-oxidation rates were expected. To investigate this, the degradation of TC was measured 20 h after treatment end and the results are reported in Figure 8. An average further TC degradation increase of 18.1% was observed in the solutions treated in flow configuration (after 20 h), while this figure was 17.4% for the solutions treated for 5 minutes, 13.9% for 10 minutes and 2.7% for 15 minutes. The reported results indicate that the rapid decrease in antibiotic concentration observed during treatment may be caused by oxidation by short-lifetime ROS, UV light and O_3 , while the further improvement in TC degradation observed after 20 h may be explained by the slower reaction of TC with the stable ROS that are still present in solution after treatment.

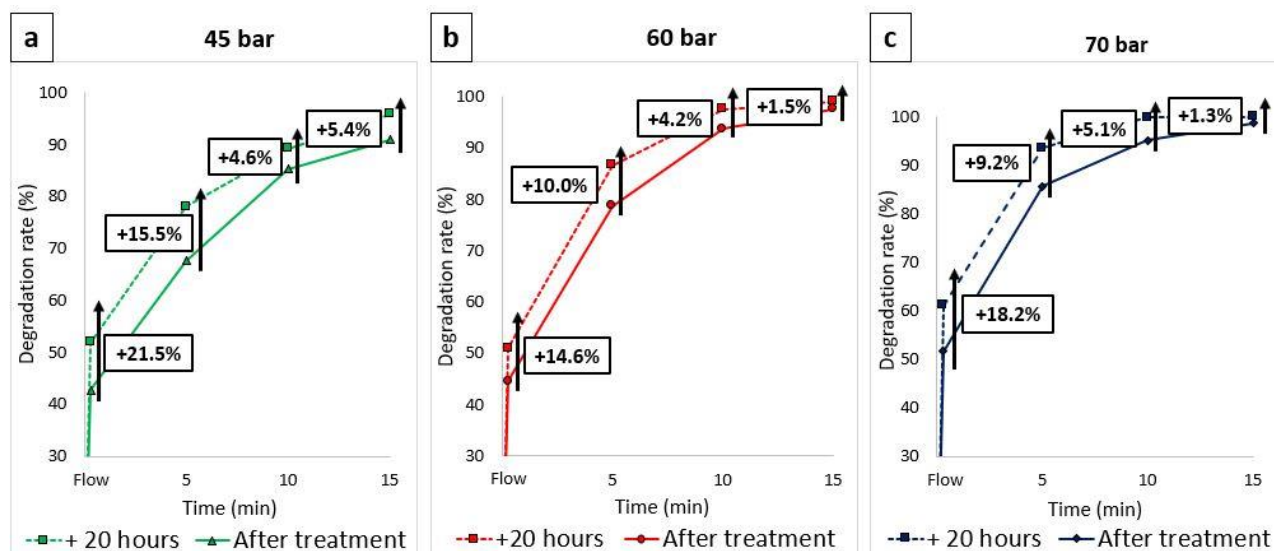


Figure 8. HC/ED long effect of generated oxidizing species on TC degradation in water. a) Inlet pressure 45 bar. b) Inlet pressure 60 bar. c) Inlet pressure 70 bar.

Although it is more sustainable to extend the treatment to 15 minutes instead of waiting 20 additional hours for the degradation of TC, this achievement could open new possibilities in advanced oxidation processes (AOPs) performed in water: a rich-ROS water solution preventively obtained with hybrid HC/ED technology could be exploited to degrade organic pollutants added to it later.

3.4 Effect of initial TC concentration on HC/ED degradation rate

The concentration of the contaminants that must be degraded plays a crucial role in the field of wastewater treatment, especially in real industrial wastewater effluents. In particular, during the development of new technologies for wastewater treatment, evaluations of their capability to treat different starting concentrations of contaminant are necessary. For this purpose and to further investigate the efficiency of the prototype reactor in degrading different starting concentrations of TC, different TC solutions (10, 25, 50, 75 and 100 mg/L) were treated at a fixed inlet pressure of 70 bar. As reported in Figure 9, the best overall degradation was observed at the end of the treatment performed on the 10 mg/L solution, especially in the flow set-up (66.5%) and after 5 minutes (99.5%). However, after 15 minutes of treatment, no particular differences in terms of degradation rate were observed between the various initial concentrations of TC, confirming the efficiency of the new prototype reactor in the versatile treatment of low, middle and high concentrations of contaminant.

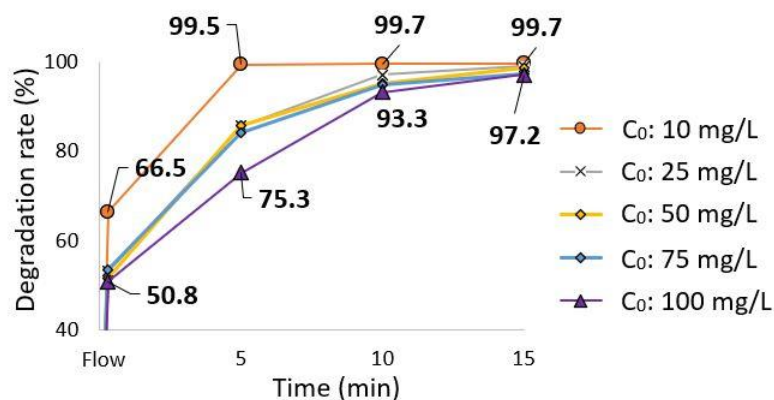


Figure 9. Effect of TC initial concentration on HC/ED degradation rate.

3.5 TC-transformation products and proposed degradation paths under different cavitation approaches

The different TC-degradation pathways that occur under various oxidative conditions (AOPs) have recently been documented in the literature.^{45,46} To the best of our knowledge, no study on the degradation products obtained after the treatment of aqueous TC solutions has ever been reported in the literature. We therefore present, herein, a HPLC-MS analysis of a HC/ED-plasma-treated TC water solution to identify the degradation products that could be seen in total ion chromatography after hybrid treatment. Moreover, the same analysis was also performed on a TC solution that underwent simple cavitation treatments; acoustic (US) and HC without coupled ED plasma. It is worth noting that different degradation products were only recorded when the technological approach was changed; HC/ED plasma vs HC or US (Figure 10, **Figures S10 and S11**). Specifically, **TC(1a)**, which is a three-ring structure with a $m/z = 274$, was the only degradation product detectable after 15 min of combined HC/ED plasma treatment. Although this degradation product, TC(1a), has already been documented in a recent study by Lee *et al.*,¹³ theirs was a strong advanced oxidation procedure that used a Fenton system based on Fe_3O_4 and persulfate for TC degradation in 60 min treatment. The same result was achieved herein by combining two advanced technologies (HD and ED plasma) without any additional catalyst or external oxidant agent. For the sake of comparison, the degradation products recorded after 15 min of HC treatment (with the ED plasma turned off) and US treatment, performed at 500 kHz, are reported (Figure 10, **Figures S5 and S6**). In accordance with the fact that HC and US granted TC-degradation values of only 50 and 18%, respectively, rather than the 98% recorded with HC/ED (Figure 3), the degradation products obtained with these strategies differ from those obtained with HC/ED, as can be observed in Figure 10, but overlap with each other in the **TC (1b)** ($m/z = 417$) and **TC (2b)** ($m/z = 358$) products. The detected **TC (1b)** is probably the result of the loss of the dimethyl amino group on the C4 of **TC** ($m/z = 445$). While the formation of the **TC (2b)** product, with $m/z = 358$, was probably the result of the first dehydration pathway, from C6 of the **TC (1b)**, followed by a deamidation reaction at C1 of TC (namely, the loss of the acylamino group).¹³ As can be observed in Figure 10, the combined HC/ED approach more quickly and effectively degraded the TC structure than HC alone or US treatment.

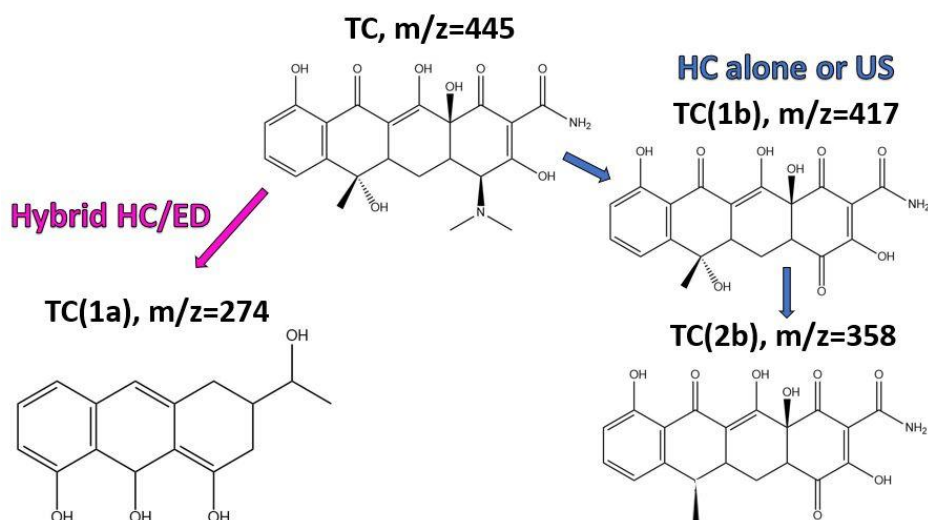


Figure 10. TC-degradation pathway under the HC/ED plasma degradation strategy vs HC or US alone.

3.6 Antibiotic-degradation screening under hybrid HC/ED treatment: TC, DC, OC.

Additional hybrid HC/ED treatments were conducted on aqueous solutions of two other kinds of TC antibiotics: OC and DC. For each antibiotic, a screening of inlet pressure was performed to evaluate its effect on the degradation treatment and, subsequently, to compare the prototype reactor's efficiency in degrading three different antibiotics of the same class. Generally, an increase in inlet pressure, from 45 bar to 70 bar, led to an increase in the degradation rate of both antibiotics, as observed and described in *section 3.2*. The highest degradation rates for OC and DC were observed after 15 minutes of treatment, and were 95.5% and 98.1%, respectively (Figure 11). The extent of degradation for the treatments performed in flow mode was higher for oxytetracycline, while higher degradation rates were observed for DC in loop configuration. This is probably because different oxidation pathways occurred for the two antibiotics. A comparison of the degradation rates of OC and DC with those of TC highlighted the fact that the extent of TC degradation was higher in both flow and loop treatment, except for when treatments were conducted for a total time of 15 minutes at 70 bar. In this case, similar levels of almost complete degradation were observed for the three antibiotics.

Several authors have performed photo-Fenton, photocatalytic and photochemical treatments for the degradation of OC without combinations or hybridization with HC. Xu *et al.*,⁴⁷ have developed a graphite carbon nitride coupled with a high-dispersed iron (II) phthalocyanine photocatalyst (CNFP), which is a Fenton-like catalyst, to enhance OC degradation in the presence of H₂O₂. They made use of 80 mL of a 10 mg/L OC solution, and obtained a maximum degradation rate of 87.5% after 60 minutes of treatment. Interesting results have also been obtained by Lopez-Penalver *et al.*,⁴⁸ who exploited a combined UV/H₂O₂ system to treat 40 mL of 20 mg/L OC solution, leading to complete degradation after only 6 minutes, in the presence of a 2 mmol/L solution of H₂O₂ at pH 2. HC technology has been exploited, both alone and in combination with a novel magnetic Z-scheme (TiO₂/Er³⁺:yAlO₃)/NiFe₂O₄ photocatalyst, by Yi *et al.*⁴⁹ In detail, HC alone, with an applied pressure of 3 bar and a 10-holed orifice place (2 mm of diameter for each hole), degraded a 10 mg/L solution of OC by a value of 40.0% after 90 minutes of treatment, while the addition of the photocatalyst, activated by a 300 W xenon lamp, allowed a maximum degradation of 73.2% to be achieved. Moving now to DC, a photocatalytic and Fenton-based treatment has been applied by Bolobajev *et al.*,⁵⁰ on a total volume of 800 mL of a 5 mg/L solution of TC, with the complete degradation of the antibiotic being observed within 15 minutes of treatment with a 3.4 mg/L solution of H₂O₂, a 0.6 mg/L solution of Fe³⁺ and UV-C radiation. Another Fenton process has been used, by Borghi *et al.*,⁵¹ for the complete degradation of DC dissolved in ultrapure water (200 mL, 100 mg/L) using a 611 mg/L solution of H₂O₂, a 25 mg/L solution of Fe²⁺ and a total treatment time of 10 minutes. DC degradation has also been performed in a combined HC and UV/Fenton

process by Tao *et al.*⁵² In detail, cavitating jets were generated by the application of an inlet pressure of 10 mPa to the recirculated and UV-irradiated DC solution in the presence of hydrogen peroxide, ferrous sulfate, copper sulfate and titanium dioxide, leading to a degradation rate of 71.2% after 60 minutes of treatment. As already discussed in *section 3.1*, the use of the hybrid HC/ED reactor means that photocatalysts and/or chemical oxidizing agents are unnecessary for the degradation of OC and DC, and that the process occurs in shorter times than those indicated in literature data.

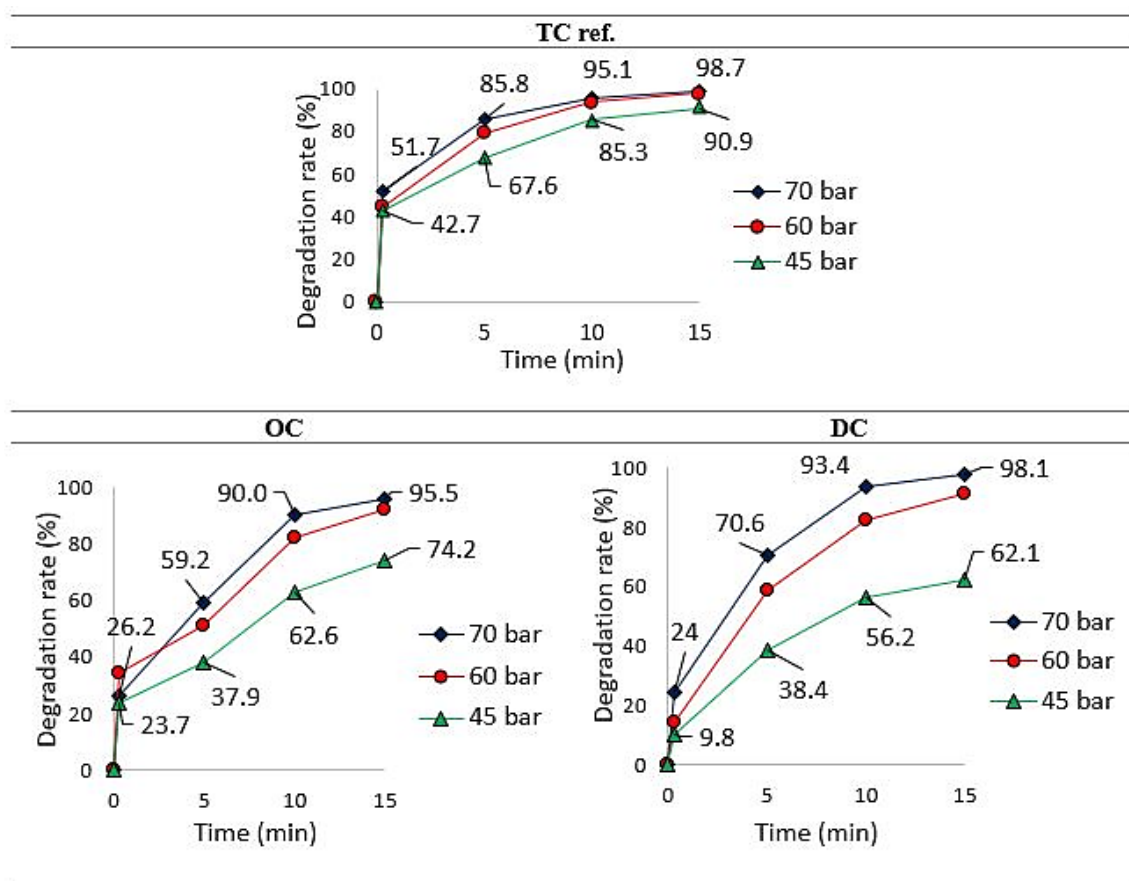


Figure 11. Antibiotic-degradation screening under hybrid HC/ED treatment: TC, DC, OC.

3.7 Influence of pH on degradation rate of TC -OX- DOX (50 mg/L) under hybrid HC/ED treatment.

TCs are amphoteric compounds, meaning that different species will predominate in water as a function of the pH. At pH 7.5–10, the monoanionic form, TC^- , is present, at pH > 10, the dianionic form, TC^{2-} , predominates, and, at pH < 4, the protonated form, TC^+ , is principally found.^{52,53} As reported by other authors,^{36,54} the TC-degradation rate for both cavitation and photochemical oxidation treatments are generally influenced by the starting pH of the water solution, leading to remarkable reductions or increases in TC removal, compared to processes performed at their natural pH. For the sake of comparison, different degradation treatments for TC, DC and OC were performed, in this work, under hybrid HC/ED at starting pH values of 2 and 11 and the best operating conditions. Neither the acid or alkaline solution conspicuously influenced the degradation rates of the three antibiotics (Figures 12 and 13). A slight increase in TC degradation was observed for short treatment times at pH of 2. However, no differences in the degradation rate were observed for pH 2 and 11 after 15 minutes, compared to the treatments performed at their natural pH values.

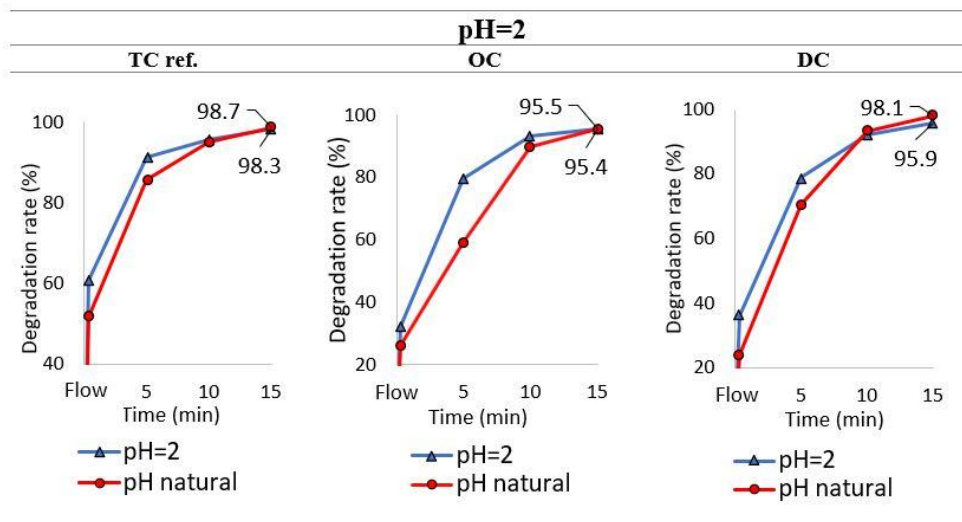


Figure 12. Influence of pH 2 on TC, OC and DC degradation under pilot-scale HC/ED plasma treatment.

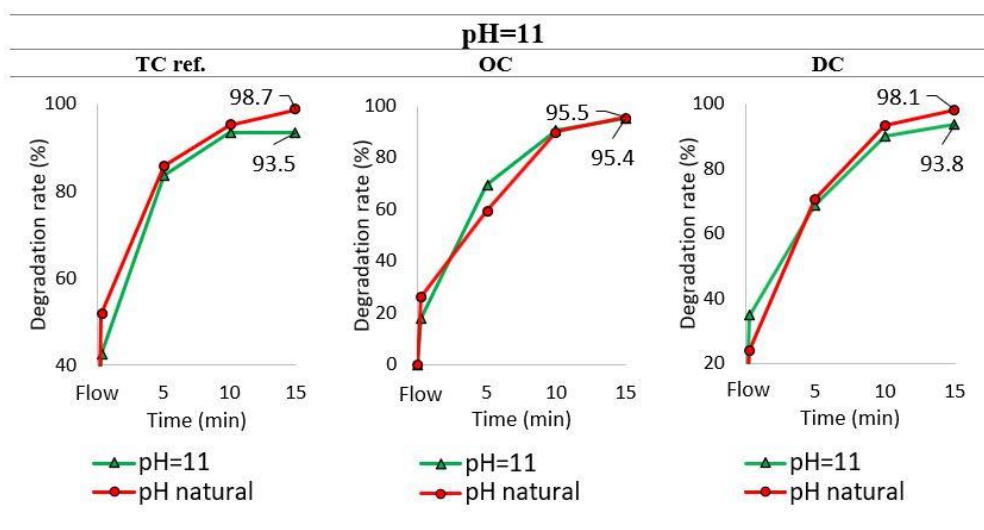


Figure 13. Influence of pH 11 on TC, OC and DC degradation under pilot-scale HC/ED plasma treatment.

Conclusion

This study presents a new understanding of the almost complete and rapid degradation of TC (> 98%) on a pilot scale using combined HC / ED plasma technology. The excellent results were achieved thanks to the synergistic effect of the cavitation and the *in-situ* generated ED plasma, which makes the use of chemical oxidants and catalysts unnecessary. Nearly quantitative TC (> 98%), DC (98%) and OC (95%) degradation was documented after only 15 min of combined HC/ED plasma treatment at 70 bar and 48 kHz. To better understand the synergistic effect of combined HC/ED treatment on antibiotic degradation, a dosimetry assay was performed to quantify the oxidizing compounds that are generated in water by this hybrid technology. Specifically, it highlighted how the coupled HC/ED plasma treatment is able to linearly increase the amount

of oxidants in water as a function of time, with a maximum concentration of 13.426 mmol/L being reached after 15 minutes. This is more than 85-times higher than the amount achieved under HC alone (0.153 mmol/L), demonstrating the effectiveness of this hybrid approach. This technology has considerable potential for the rapid and sustainable degradation of recalcitrant antibiotics in wastewater without the need for external catalysts and oxidants.

Associated Content

Supporting Information

The Supporting Information is available:

General pilot-scale HC/ED experimental set up and procedure for cycline degradation; Pilot scale HC/ED hybrid reactor: HC chamber working in HC alone mode; Video of pilot scale HC/ED hybrid reactor working in HC alone mode; Pilot scale HC/ED hybrid reactor: HC chamber working in HC/ED hybrid mode; Video of pilot scale HC/ED hybrid reactor working in HC/ED hybrid mode; General “lab-scale HC” experimental set up and procedure for cyclines degradation; General procedure for cyclines analyses; Spectrophotometric analysis; Calibration curves of TC, DC and OC at pH 2 and 11; Chemical oxygen demand (COD) analysis; Monitoring of degradation rate and COD of TC treated in the pilot scale HC/ED reactor in deionized water with an inlet pressure of 60 bar; Cavitation yield evaluation: Degradation rate and cavitation yield of treatments performed in deionized water and tap water; MS spectrum of TC treated under pilot scale HC/ED; MS spectrum of TC treated under lab scale HC or US bath.

Acknowledgments

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