

Research Article

Degradation of Antibiotics in Wastewater during Sonolysis, Ozonation, and Their Simultaneous Application: Operating Conditions Effects and Processes Evaluation

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Pharmaceutical drugs frequently found in treated effluents, lakes and rivers, can exhibit adverse effects on aquatic organisms. The present study focuses on the application of advanced oxidation processes as ozonation (O_3), sonolysis (US), and their combined application ($US+O_3$) for the degradation of diclofenac in wastewater. Under the applied conditions, all three systems proved to be able to induce diclofenac oxidation, leading to 22% of mineralization for O_3 and 36% for US process after 40 min of treatment. The synergy observed in the combined schemes, mainly due to the effects of US in enhancing the O_3 decomposition, led to a higher mineralization (about 40%) for 40-minute treatment and to a significantly higher mineralization level for shorter treatment duration.

1. Introduction

The widespread occurrence of pharmaceuticals and personal care products in the aquatic environment is a recognized problem of unknown consequences [1–3]. Different sources may cause the appearance of pharmaceuticals in water and soils. The main one is represented by wastewater treatment plants (WWTPs) effluents [4, 5]. Other sources include direct applications in aqua farming, manure run-off [1], via hospital effluent [6], or finally, via landfill leaching [7]. In the aquatic environment, diclofenac (DCF) is one of the most frequently detected pharmaceuticals [8]. Its presence in urban wastewater treatment plants (UWTPs) effluents has been often documented [3, 9–12], with a usual concentration ranging from 2 to 10 $\mu\text{g/L}$ [1, 3, 5, 6].

Recent studies revealed that conventional water treatment processes cannot completely remove DCF from source waters [13–17], so the adoption of advanced oxidation processes (AOPs) in the tertiary treatment section of existing UWTPs can significantly represent a tool for this reduction [12, 17–21].

Several AOPs have been evaluated for the degradation of diclofenac. A number of studies indicated a high reactivity of DCF towards ozonation [12, 13, 17, 21, 22]. In [22], Authors also noted a positive effect of hydrogen peroxide addition on the diclofenac conversion by ozone.

In a different work [20], the H_2O_2/UV treatment of DCF has been investigated, and the obtained results have been compared with ozonation and direct photolysis. At an initial DCF concentration of 296 mg/L, direct photolysis ensured a drug removal up to 45% for a treatment time of 1.5 h using a 17-W low-pressure Hg lamp that emitted UV light at 254 nm with an intensity of $2.7 \cdot 10^{-6}$ Einstein/s.

The DCF degradation was strongly enhanced by the addition of hydrogen peroxide (170 mg/L; H_2O_2/UV AOP) to more than 90% conversion. The Fenton-type process has had an apparent disadvantage during the DCF degradation because the drug ($pK_a = 4.15$) precipitated in an acidic medium, which is required to keep iron dissolved [23, 24]. Titanium dioxide photocatalysis induced by UV-A [25, 26] or artificial solar irradiation [24, 27] was also evaluated for the DCF degradation.

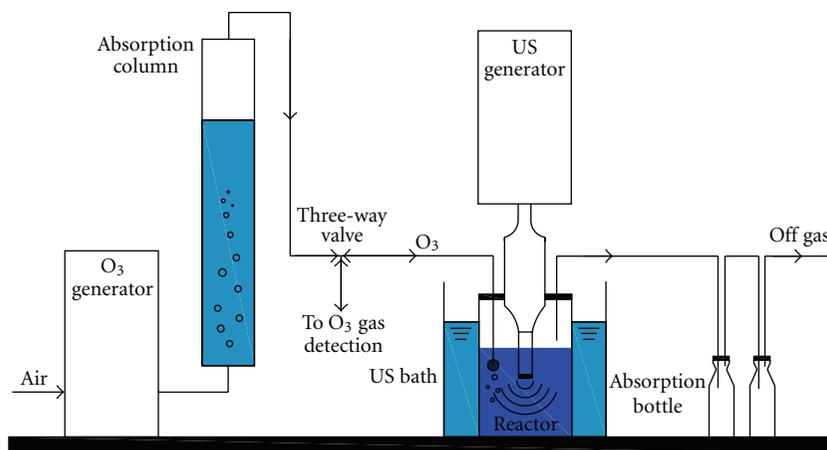


FIGURE 1: Laboratory-scale experimental setup for the degradation of diclofenac through ozonation/sonolysis.

DCF sonochemical degradation in synthetic water has been analyzed only in recent times [28–30].

Among the mentioned processes, sonolysis, ozonation, and their combined application have been investigated in this study as suitable tools for pharmaceutical degradation from UWTPs effluents.

The application of ultrasound technology to wastewater treatment has been developed in recent times [28, 31–36]. The sonolysis of aqueous solutions, based on cavitation with high temperatures and pressures, leads to the formation of highly reactive hydroxyl radicals ($\cdot\text{OH}$).

The main objective was to investigate and compare the effects of ultrasound (US), ozone (O_3), and their combination (US+ O_3) on DCF degradation, with the analysis of operating parameters such as pH, temperature, US power density, and O_3 dose.

2. Materials and Methods

2.1. Reagents. DCF (crystalline sodium salt of [2-(2,6-dichlorophenylamino)-phenyl]-acetic acid), characterized by a solubility in water of 237 mg/L at 25°C and a melting point of 275–277°C, was provided by Sigma-Aldrich.

Tests were performed on urban wastewater samples (Table 1), in which a known concentration of DCF was spiked.

According to reported concentration levels in drug industry wastewater, the spiked concentrations were considerably higher than DCF occurrence levels in the environment, but these concentrations were intentionally selected so as to be able to better monitor the removal and mineralization potential with available analytical techniques [6, 17, 26, 29, 34].

2.2. Experimental Setup. Ozone was generated onsite by an O_3 supply system (Microlab, Aeraque, Italy) using ultrapure air. The air flow rate to the ozone generator was monitored with a rotameter. Ozone flow was controlled using an absorption column containing deionised water. Surplus ozone

TABLE 1: Physicochemical characterization of sampled wastewater (WWTP effluent).

Parameter	Average value
pH	8.10 ± 0.98
DO (mg/L)	5.30 ± 1.03
Electrical conductivity ($\mu\text{S}/\text{cm}$)	1696 ± 182
Turbidity (NTU)	0.827 ± 0.158
BOD ₅ (mg/L)	7 ± 2
COD (mg/L)	8.6 ± 3
TOC (mg/L)	4.51 ± 1.62

was passed into gas absorption bottles containing 2% (w/v) KI solution.

The US tests were carried out with a Sonics Vibracell VCX-750 (Sonics & Materials Inc., USA) ultrasonic transducer, equipped with a 20 kHz converter and a titanium horn with a 1.3 cm in diameter tip. During the tests, the probe was partially immersed in the liquid for about 4 cm, fixed at the centre of the reactor, and plugged with a polyethylene cap during the operation. The ultrasonic process was performed into an ultrasonic bath in order to keep the temperature constant over time. In Figure 1, a scheme of the experimental setup at laboratory scale is provided.

Combined US+ O_3 tests were carried out using a combined ozonation and sonolysis experimental setup as detailed in [29]. In all tested conditions, a spiked wastewater solution (150 mL), contained in a 250 mL cylindrical Pyrex glass reactor (Schott Duran, Germany), was used.

2.3. Experimental Conditions. The ozonation tests were conducted at different treatment duration (i.e., 5, 10, 20, and 40 min), using two different ozone flows (2.4 and 31 g/h), which were able to keep dissolved ozone concentrations in the 5–15 mg/L range, similar to those already used for disinfection and other compounds removal [17, 37, 38].

Ozone was generated onsite by an O_3 supply system (Microlab, Aeraque) using ultrapure air. The air flow-rate to

the ozone generator was monitored with a rotameter. Ozone flow was controlled using an absorption column containing bidistilled water. Surplus ozone was passed into gas absorption bottles containing 2% (w/v) KI solution.

The US tests were carried out with (TC) and without (NTC) temperature control, under varying treatment duration (i.e., 15, 30, 45, and 60 minutes), using power densities of 100, 200, and 400 W/L. In TC tests, sample temperature was maintained constant at $20 \pm 3^\circ\text{C}$ using an appropriate ultrasonic bath. To compare the experimental results obtained with O_3 and combined US+ O_3 processes, tests were also repeated at the same treatment duration (i.e., 5, 10, 20, and 40 min), using the optimum investigated sonolysis conditions (NTC, 400 W/L).

The combined US+ O_3 tests were also carried out at varying duration (i.e., 5, 10, 20, 40 min), using an ozone flow of 31 g/h and a 400 W/L power density according to the best ozonation and sonolysis results in distinct applications.

2.4. Analytical Methods. DCF conversion was assessed in terms of TOC and UV absorbance. A UV-Vis spectrophotometer equipped with a 1 cm quartz cell (Lambda 12, Perkin Elmer) was used for the absorbance measurements and the determination of the DCF spectrum with a characteristic peak at 276 nm (UV276), which is the wavelength that corresponds to the maximum absorbance and gives a sufficient indication of each drug's concentration [26]. The assumption that some of the by-products formed during the oxidation could also absorb at the same wavelength should of course be considered. However, in that case, the conversion of the parent compounds obtained in this study would have been even higher. Therefore, despite this assumption, UV absorption measurements provide a quick and indicative determination of the conversion.

These measurements were used as a fast and preliminary assessment of the compound behaviour [26, 29, 34]. TOC values were detected by a TOC analyzer (Shimadzu TOC-5000A). Water parameters such as pH, turbidity, conductivity, dissolved oxygen, and temperature were also detected before and after treatment in each test by a multiparameter equipment (HANNA Instrument, USA). Dissolved ozone concentrations in water and ozone flows were measured according to procedures described in AWWA-APHA-WEF Standard Methods 4500- O_3 and 2350-E. The off-gas ozone was trapped in a KI solution scrubber to quench ozone. DCF mineralization was due to oxidation reactions that involved the original compound at first, and then its by-products that had been gradually formed.

3. Results and Discussion

3.1. Ozonation. During ozonation tests, its effect on various physicochemical properties of the solutions was investigated. In all tested conditions, electrical conductivity increased versus treatment duration (initial DCF concentration = 40 mg/L, ranging from 10 to 157 mg/L for 40 min treatment time), while pH was reduced to low values (pH = 3-4). Figure 2 shows the DCF concentration decrease, in terms

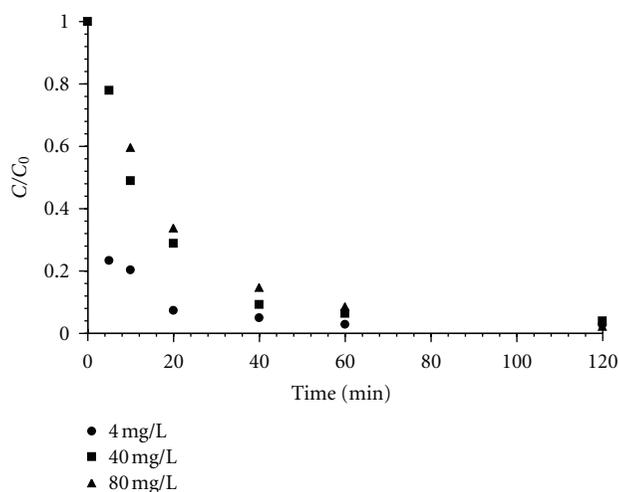


FIGURE 2: Comparative rates of diclofenac decay, in terms of absorbance, by ozonation (ozone flow = 31 g/h).

TABLE 2: Ozonation: degradation rate constants (k , K) for three different DCF concentrations.

Spiked DCF (mg/L)	Absorbance		TOC	
	k (L/(mg·min))	R^2	K (mg/(L·min))	R^2
4	2.652	0.789	0.006	0.961
40	0.166	0.977	0.106	0.960
80	0.126	0.879	0.293	0.794

of absorbance (UV₂₇₆), in relation to both ozonation time and initial concentration of DCF. For the highest O_3 flow (31 g/h), DCF degradation is approximately exponential versus ozonation time, with an almost complete DCF removal after 40 minutes, even at high initial DCF concentrations. Reducing the ozone flow, the DCF degradation versus time was reduced, this being even more evident when the DCF concentration was increased. The DCF degradation was certainly not due to its stripping by the ozone flow because of its Henry coefficient low value, equal to $3 \cdot 10^{-3} \text{ Pa} \cdot \text{m}^3/\text{mol}$ at 25°C [39]; instead, it was probably due to hydrogen peroxide formation, because of the direct reactions of ozone with DCF and its aromatic and unsaturated organic intermediates formed during the initial stage of the process [17].

At higher DCF concentrations (40 and 80 mg/L), ozonation followed a second-order kinetic. Depending on the pharmaceutical initial dose, the apparent rate constants (k , K) are reported in Table 2. The removal rate significantly increased when the DCF initial concentration was reduced. At DCF initial concentration of 4 mg/L, a significant pharmaceutical reduction was achieved at very short treatment durations (10 min).

The initial degradation rate was approximately linear versus initial DCF concentration. Reducing the ozone flow, the pharmaceutical degradation was decreased versus time, so different runs were compared using the initial conversion rate (ICR) referred to the first 20 minutes (Figure 3).

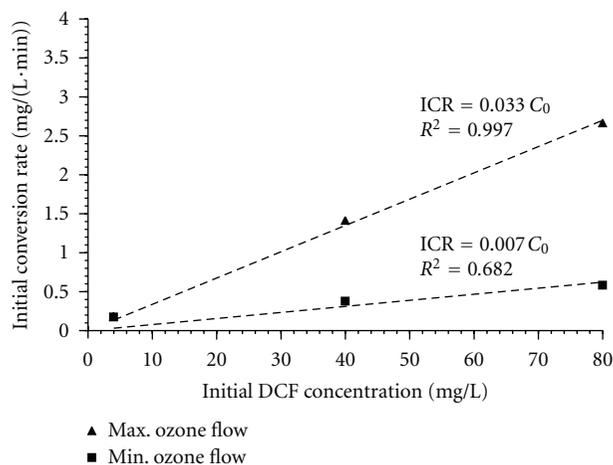


FIGURE 3: Initial DCF conversion rates, in terms of absorbance, by ozonation (ozone flow = 31 g/h).

The fact that the compound reacts so fast with ozone makes more necessary the process analysis in terms of TOC reduction that represents in a better way the real capacity of ozone to deal with DCF and its by-products mineralization. TOC removal behaviour was linear in relation to the ozonation duration and increased with initial DCF concentration (Figure 4). Although UV absorbance measurements indicated complete drug removal after 40 minutes, the maximum TOC reduction achieved was only 30% for an initial DCF concentration of 80 mg/L.

This result, as documented in the literature about organic compound ozonation [17, 40, 41], can be probably attributed to the formation of secondary organic by-products (carboxylic acids such as maleic, malonic, pyruvic, and oxalic acids), with some polar character, which did not react with ozone and showed a different UV absorbance profile than that of the parent compound [29, 30, 34].

3.2. Sonolysis. During sonication tests, the effect on the treatment efficiency of physicochemical properties of tested solutions has been investigated. In all analyzed conditions, electrical conductivity was increased, while pH and redox potential were reduced by the sonication treatment duration. However, the behaviour of these parameters was strongly influenced by the ultrasonic power dose [33].

The DCF concentration decline, in terms of TOC, is shown in relation to irradiation time and US density in Figure 5.

Since the DCF salt is considerably soluble in water and nonvolatile, degradation inside the cavitation bubble was insignificant, and therefore, hydroxyl radical-induced reactions were likely to be the main DCF degradation mechanism. Hydroxyl radicals, formed through water sonolysis, can partly recombine yielding hydrogen peroxide which in turn reacts with hydrogen to regenerate hydroxyl radicals. Therefore, the showed results (Figure 5) are, perhaps, directly connected to the hydroxyl radicals action, which increased when high ultrasound densities were applied. A higher

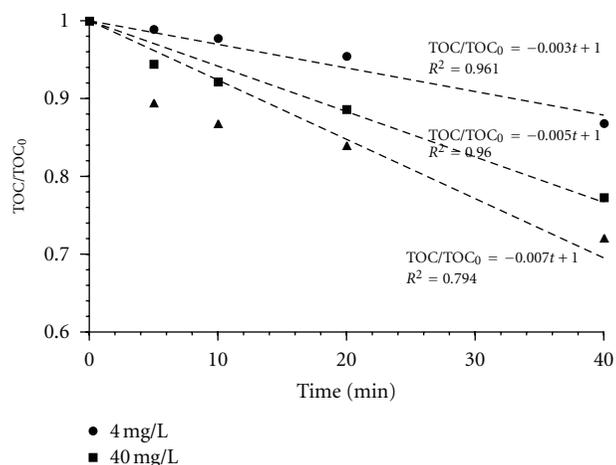


FIGURE 4: Comparative rates of diclofenac organic carbon decay in terms of TOC by ozonation (ozone flow = 31 g/h).

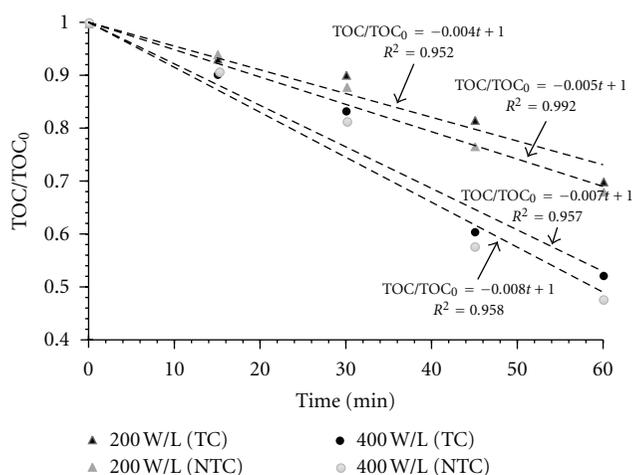


FIGURE 5: DCF degradation in terms of TOC in relation to ultrasound power densities and bulk temperature conditions (20 kHz, $C_0 = 40$ mg/L).

US density results in higher supply energy that leads to an enhanced formation of cavitation bubbles. Hence, the degradation rate of DCF increased with the power density.

In NTC conditions, a gradual temperature increase of the liquid bulk solution was recorded due to heat dissipation. For the experiments performed at 400 W/L, temperature increased from 25°C at $t = 0$ to 71°C at 30 min and finally to 76°C at 60 min; the corresponding values at 200 W/L were 66 and 71°C. Consequently, increased temperatures favour DCF conversion: in NTC tests, more than 55% of DCF was degraded by a 400 W/L power density within 60 min, at initial concentration of 80 mg/L.

At 100 W/L, the DCF degradation rate was quite low, whereas only small differences between the degradation rate at 200 and 400 W/L were observed. Since the maximum temperature obtained during the bubble collapse is proportional to the liquid bulk temperature, increased temperatures are expected to enhance reaction rates. Nevertheless, this effect

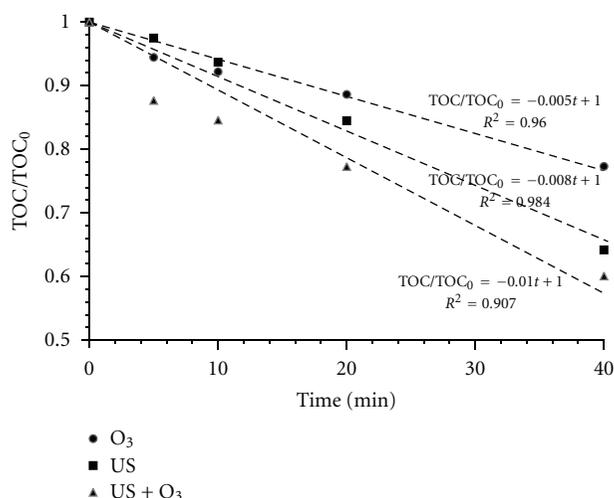


FIGURE 6: Comparative rates of diclofenac ($C_0 = 40$ mg/L) organic carbon decay in terms of TOC in 40 min by sonolysis (20 kHz, 400 W/L, NTC), ozonation (31 g/h), and their simultaneous application (US+O₃).

can be counterbalanced or even overcome by the fact that bubbles contain more vapour, which moderates implosion and consequently reduces reaction rates. However, in NTC conditions, the increase in liquid bulk temperature resulted in an increase in DCF conversion; therefore, during TC tests, the pharmaceutical degradation was always lower.

3.3. Combined US+O₃ Treatment. The US+O₃ tests were carried out through the combination of the sonolysis and ozonation optimized removal conditions, which were obtained through the former experimental runs (31 g/h O₃ flow, at 400 W/L ultrasonic power density, without temperature control). During US+O₃ tests, the initial solution temperature and electrical conductivity increased versus treatment time. As for sonolysis and ozonation, pH was instead reduced from a nearly neutral to acidic values (pH = 3-4).

In terms of absorbance, DCF degradation can be described by a first order reaction kinetic. The removal rate increased significantly when comparing the ozonation treatment efficiency to the combined US+O₃ process. In terms of absorbance measurements, the final DCF concentration in solution is probably the same (about 3 mg/L) for 40 minutes, in both cases, but for 5 to 20 minutes the combined US+O₃ action induced much higher degradation.

TOC measurements showed linear trends (Table 3). For 40-minute treatment, DCF reduction was up to 39%, greater than the degradation attributable to ozonation (22%), and comparable with those due to sonolysis (36%). During the first 20 minutes of the experiment, the combined US+O₃ action induced significantly higher TOC removal (Figure 6).

4. Conclusions

The persistence in the environment of DCF and its oxidative degradation by means of ozone, ultrasound, and their

TABLE 3: DCF degradation rate constants (K) in terms of TOC referred to sonolysis (20 kHz, 400 W/L, NTC), ozonation (31 g/h), and their combination (US + O₃) for an initial DCF concentration of 40 mg/L.

Treatment process	TOC	
	K (mg/(L·min))	R^2
US	0.169	0.984
O ₃	0.106	0.960
US + O ₃	0.211	0.907

simultaneous application has been studied in the present work. The ozonation has been demonstrated to be a suitable tool for pharmaceuticals degradation in wastewater samples even at process conditions usually adopted in drinking water facilities. Sonolysis is more efficient than ozonation for the mineralization of DCF. Results show that there is a synergistic effect when sonolysis and ozonation are applied jointly, and this is attributed to the enhanced O₃ degradation by collapsing bubbles that may yield additional free radicals. The degradation pattern of high concentrations of DCF in wastewater is similar for all tested processes.

The results obtained through this research work can be further enhanced through the investigation of the by-products formation by chromatographic techniques, in order to better determine and assess the removal kinetics of the formed compounds. In addition, toxicity bioassays can help in the evaluation of the potential impact that these by-products may exhibit. It is also necessary to implement the combined processes at a pilot scale to better assess the pharmaceuticals degradation in real wastewater samples.

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