

Removal of pharmaceuticals using combination of UV/H₂O₂/O₃ advanced oxidation process

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ABSTRACT

Water and wastewater effluents contain a vast range of pharmaceutical chemicals. The present study aims to determine the potential of the advanced oxidation technology UV/H₂O₂/O₃ and its sub-processes (i.e. UV, UV/H₂O₂, UV/O₃, O₃ and H₂O₂/O₃) for the degradation of the antibiotics ciprofloxacin (CIP) and trimethoprim (TMP), and the antineoplastic drug cyclophosphamide (CPD) from water. Creating AOP conditions improved in most cases the degradation rate of the target compounds (compared to O₃ and UV alone). H₂O₂ concentration was found to be an important parameter in the UV/H₂O₂ and H₂O₂/O₃ sub-processes, acting as [•]OH initiator as well as [•]OH scavenger. Out of the examined processes, O₃ had the highest degradation rate for TMP and H₂O₂/O₃ showed highest degradation rate for CIP and CPD. The electrical energy consumption for both CIP and CPD, as calculated using the E_{EO} parameter, was in the following order: UV > UV/O₃ > UV/H₂O₂/O₃ > O₃ > H₂O₂/O₃. Whereas for TMP O₃ was shown to be the most electrical energy efficient. Twelve degradation byproducts were identified following direct UV photolysis of CIP.

Key words | advanced oxidation, byproducts, EEO, ozone, pharmaceuticals, photodegradation, photolysis

INTRODUCTION

Chemicals as prescription drugs, contraceptive pills, household chemicals, detergents and cosmetics are excreted or discharged by humans as wastewater contaminants. Commonly used wastewater treatments do not sufficiently remove these contaminants, thus they may still remain in trace concentrations in the treated effluents. As a result, effluents containing micro-pollutants like pharmaceuticals enter rivers, groundwater and drinking water by direct discharge, irrigation or artificial recharge. Several studies conducted world-wide have confirmed the occurrence of pharmaceutical residues in wastewater treatment plants (WWTPs) (e.g. Hirsch *et al.* 1999), water streams (e.g. Kolpin *et al.* 2002), surface and ground-waters (e.g. Avisar *et al.* 2009).

The acute and chronic effects of pharmaceutical compounds on the ecosystem and on human health are not yet fully understood, yet the problem remains worrisome, due to many concerns as the possible development of antibiotic-resistance bacteria. Other concerns rise from the presence of toxic pharmaceuticals as antineoplastic drugs that are used in cancer chemotherapy. These drugs, typically originated from hospital wastewater, even though detected

in the environment at much lower concentrations in relation to other drugs, cannot be excluded as potential environmental contaminants due to their often carcinogenic and mutagenic properties (Kummerer 2001).

An attractive technology for the treatment of pharmaceuticals in water is the advanced oxidation process (AOP), where pollutants are chemically oxidized by a process that produces hydroxyl ([•]OH) free radicals. The hydroxyl radicals can be generated, for example, by the combined application of ozone/hydrogen peroxide (O₃/H₂O₂), ultraviolet radiation/ozone (UV/O₃), UV/titanium dioxide (UV/TiO₂) or UV/H₂O₂. Rosal *et al.* (2008) found AOP technologies (e.g. O₃/H₂O₂) to be efficient in the degradation of 33 organic compounds, treating effluent from two municipal WWTPs. Other researches have demonstrated the potential of UV/H₂O₂ (Vogna *et al.* 2004; Lester *et al.* 2010) and UV/O₃ (Peyton & Glaze 1988) for the removal of different pharmaceuticals and other micro-pollutants from water and wastewater effluents. Among the O₃ and UV based AOPs, the combination of UV, O₃ and H₂O₂ (UV/H₂O₂/O₃) which employs several direct and indirect degradation

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mechanisms may present an attractive option for the degradation of a wide range of refractory pollutants. Several researches has already demonstrated the advantage of UV/H₂O₂/O₃ over other AOPs in the degradation of phenol (Kusic *et al.* 2006) and 2-propanol (Wu *et al.* 2008) from water. However, information on this complex process and its potential in degrading pharmaceutical compounds is still lacking. Therefore, the objective of the current research is to determine the potential of the UV/H₂O₂/O₃ process for the degradation of commonly used pharmaceuticals, the antibiotics ciprofloxacin (CIP) and trimethoprim (TMP), and the antineoplastic drug cyclophosphamide (CPD). More specifically, this study aims to evaluate the efficiency of each of the sub-processes composing the UV/H₂O₂/O₃ process, namely: UV, O₃, UV/H₂O₂, UV/O₃, H₂O₂/O₃ and UV/H₂O₂/O₃, on the degradation of the selected pharmaceuticals.

METHODS

Chemicals

Pharmaceutical standards (>99% purity) were obtained from Sigma-Aldrich, ULC grade acetonitrile and water from Bio-Lab Ltd. (Jerusalem, Israel). All chemicals were used as obtained and pharmaceutical stock solutions were prepared by dissolving the compounds in deionized water (Direct-Q3 UV system, Millipore-France) at a concentration of 100 mg/L. H₂O₂ (30% w/w, extra pure) was obtained from Merck (Germany). Unless otherwise mentioned, all experiments were conducted in 2.5 mM phosphate buffer saline (PBS) at pH 7.

Experimental setup

UV Collimated Beam Apparatus (CBA)

A bench scale CBA was used to study the UV/H₂O₂ process (described in details elsewhere; Lester *et al.* 2010). In the CBA experiments, UV light is directed through a collimated tube to dose a sample solution. Experiments were carried out using a 0.45 kW medium-pressure (MP) polychromatic UV lamp emitting wavelengths at the range of 200–300 nm and beyond (Ace-Hanovia Lamp). The spectral incident irradiance obtained from a calibrated spectroradiometer (USB4000, Ocean Optics, FL, USA) was used to calculate the average irradiance and UV fluence (Bolton & Linden 2003).

UV/H₂O₂/O₃ batch reactor

UV, O₃, UV/O₃, H₂O₂/O₃ and UV/H₂O₂/O₃ experiments were performed in a temperature controlled (25 °C) 1 L glass cylindrical batch reactor. The center of the reactor is occupied with a quartz tube in which a 0.45 kW UV MP lamp is placed vertically (Ace-Hanovia). Ozone is generated from pure oxygen (>99.9%) through an ozone generator (2–5 g/h, OZO-1VTT, Ozomax, Canada) and introduced into the aqueous solution using a diffuser located at the bottom of the reactor, while another tube carries the off-gases from the headspace of the reactor to the ozone destructor. The solution is continuously mixed with a magnetic stirrer. Dissolved ozone was quantified using the Indigo method (Bader & Hoigne 1981).

Determination of pharmaceutical rate constants with O₃

Two different approaches were applied to determine the second-order rate constant values of the pharmaceuticals with molecular ozone ($k_{O_3,C}$, M⁻¹ s⁻¹). For CPD, with an expected low reactivity toward O₃, experiments were conducted in the 1 L reactor in a full batch mode using O₃ in excess. Ozone was initially diffused into a solution containing *t*-butanol – an •OH radical scavenger (10 mM) until the dissolved O₃ concentration reached 5 mg/L. Ozone diffusion was then stopped and CPD was injected (1 mg/L). Samples were withdrawn at appropriate time intervals, quenched with sodium thiosulfate, and analyzed with HPLC/MS. The rate constant of CPD with ozone was obtained by using the Equation below:

$$-\frac{d[\text{CPD}]}{dt} = k_{O_3, \text{CPD}} [\text{O}_3] \times [\text{CPD}]$$

$$\Rightarrow \ln \frac{[\text{CPD}]_t}{[\text{CPD}]_0} = -k_{O_3, \text{CPD}} \int_0^t [\text{O}_3] dt \quad (1)$$

where, [CPD]₀ and [CPD]_t are initial CPD concentrations (M) and its concentration after exposure time *t* (s), $k_{O_3, \text{CPD}}$ is the second-order rate constant of CPD with molecular ozone (1/M s) and the time integral over O₃ concentration is the measured ozone exposure (M s).

For the highly ozone reactive CIP and TMP, competition kinetic (CK) procedure was used, where carbamazepine (CBZ) was selected as a reference compound due to its known rate constant with O₃ ($k_{O_3, \text{CBZ}} = 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; Huber *et al.* 2003). In the CK experiments,

different understoichiometric doses of O₃ (at a range of 0.6–3.8 μM) were added separately to samples containing *t*-butanol (10 mM) and equal concentrations of the target and the reference compound (~3.5 μM each). The samples were continuously mixed during the experiments and the remaining concentrations of the target and reference compounds were analyzed by HPLC/MS. The second-order rate constants with ozone were then calculated as described below (Huber *et al.* 2003):

$$\ln \frac{[C]_H}{[C]_0} = \ln \frac{[CBZ]_H}{[CBZ]_0} \times \frac{k_{O_3,C}}{k_{O_3,CBZ}} \quad (2)$$

where, $k_{O_3,CBZ}$ ($3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, Huber *et al.* 2003) and $k_{O_3,C}$ are the rate constants of O₃ with CBZ and the target compound, respectively. H represents the different applied O₃ doses.

Determination of pharmaceutical rate constants with ·OH

The second-order rate constant of the pharmaceuticals with ·OH radical ($k'_{OH,C}$, $\text{M}^{-1} \text{ s}^{-1}$) was calculated in the UV/H₂O₂ CBA using the CK procedure (Elovitz *et al.* 2008), where *p*-chlorobenzoic acid (*p*CBA) was used as a reference compound due to its low direct photolysis rate. In brief, a mixture of the target pollutant and reference compound (at 1 mg/L each) was exposed to UV irradiation with and without H₂O₂ (50 mg/L). Samples were withdrawn at two minute intervals for HPLC/MS analysis. In cases where the reaction with ·OH is the only degradation process (no direct photolysis), CK was used in its simplest form (Equation (2)). However, when direct photolysis played a significant role in the pollutant's UV/H₂O₂ degradation, a correction was made to subtract the loss of the compound due to direct photolysis (Equation (3); Elovitz *et al.* 2008).

$$k'_{OH,C} = \frac{(k_{obs,C} - [E_{avg}(H_2O_2)/E_{avg}(w/o H_2O_2)] \times k_{d,C})}{k_{obs,pCBA}} \times k'_{OH,pCBA} \quad (3)$$

where, $k_{d,C}$ is the pollutant's time-based pseudo-first-order direct photolysis rate constant (1/s), $k_{obs,C}$ and $k_{obs,pCBA}$ are the observed (total) time-based pseudo-first-order rate constants (1/s) for degradation of the target pollutant and *p*CBA respectively. $k'_{OH,C}$ and $k'_{OH,pCBA}$ are the second-order rate constants of the target pollutant and *p*CBA with ·OH ($k'_{OH,pCBA} = 5 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$; Buxton *et al.* 1988). $E_{avg}(H_2O_2)/E_{avg}(w/o H_2O_2)$ is the ratio of the average

fluence rate with and without H₂O₂. This term is basically a weighting factor correcting for the pollutant's direct photolysis in the presence of H₂O₂.

Pharmaceutical degradation experiments

UV/H₂O₂ experiments using the CBA

The tested pharmaceuticals were prepared in 100 mL at an initial concentration of 1 mg/L. Different concentrations of H₂O₂ were added to generate the AOP process. Irradiation was performed with gentle stirring in a 7 × 5 cm crystallization dish open to the atmosphere. Samples of 0.5 mL were withdrawn at appropriate intervals for HPLC/MS analysis.

UV/H₂O₂/O₃ experiments using the 1 L batch reactor

All experiments were conducted in a semi-batch mode, where the ozone stream was continuously introduced into the aqueous solution. Initial pharmaceutical concentration was 1 mg/L. For the UV alone experiments, the UV lamp was preheated for 2 min before injecting the target compound. In O₃ and H₂O₂/O₃ experiments, steady dissolved O₃ concentration was initially achieved prior to injection of the target compound and H₂O₂. For the UV/O₃ and UV/H₂O₂/O₃ experiments, steady dissolved O₃ concentration was achieved prior to preheating UV lamp and injection of the target compound and H₂O₂. Samples (2 mL) were taken periodically after an initial mixing time of ~10 s, using a 20 cm syringe, quenched immediately with excess of sodium thiosulfate to decompose residual O₃ and analyzed chromatographically.

Analytical methods

All pharmaceuticals were detected and quantified by HPLC-UV Agilent, model 1100 (ACE-RP C18 column 2.5 mm × 250 mm) and mass spectrometer (MS) detector (Finnigan LCQ). The HPLC consists of a binary pump, microvacuum degasser, diode array detector and thermostatic column compartment. The column temperature was 32 °C, flow rate of 0.5 mL/min and injection volume of 100 μL. Positive electro-spray ionization MS mode was used where probe temperature was 220 °C. The flow from the HPLC was passed through a split connector with 60 μL/min of effluent introduced into the MS interface. Ions in the range 200–400 m/z were registered in the conventional scanning mode. For CIP and TMP, the HPLC mobile phase conditions were adapted from Lester *et al.* (2010)

with minor modifications. For CPD the mobile phase was ammonium formate 0.05 M (A) and methanol (B), at pH 5. The mobile phase eluent gradient started with 50% of eluent A followed by a 2.5-min linear gradient to 30% of eluent A, 3 min isocratic elution and a 2 min linear gradient back to 50% of eluent A, maintained for 4 min to equilibrium time. For the detection of the CIP photo-products, irradiated samples were pre-concentrated by factor of 10 using lyophilization.

RESULTS AND DISCUSSION

Determination of pharmaceutical rate constants with O₃ and [•]OH

Table 1 summarizes the measured rate-constants for the three pharmaceuticals with O₃ and [•]OH and the used methods. Of the three compounds, TMP exhibits the highest reaction rate constants with both O₃ and [•]OH, while CPD reacts slowest.

The measured rate constants in the present study agree well with previously published results. The difference in rate constants between the three pharmaceuticals is due to basic structural differences. For example, the high rate constant of TMP with molecular O₃ is attributed to the presence of several amino moieties which react rapidly with O₃ (Huber *et al.* 2003).

Pharmaceutical degradation by UV/H₂O₂

Time based degradation of the studied pharmaceuticals by UV/H₂O₂ using the CBA, with and without addition of 50 mg/L H₂O₂, is shown in Figure 1. The fluence-based rate constants were additionally calculated to be 5.8×10^{-3} , 3.4×10^{-4} and 2.3×10^{-5} cm²/mW for CIP, TMP and CPD respectively. Under direct UV light (no H₂O₂) CIP degradation rate was highest, while CPD only slightly degraded with UV. The differences in direct photodegradation rates

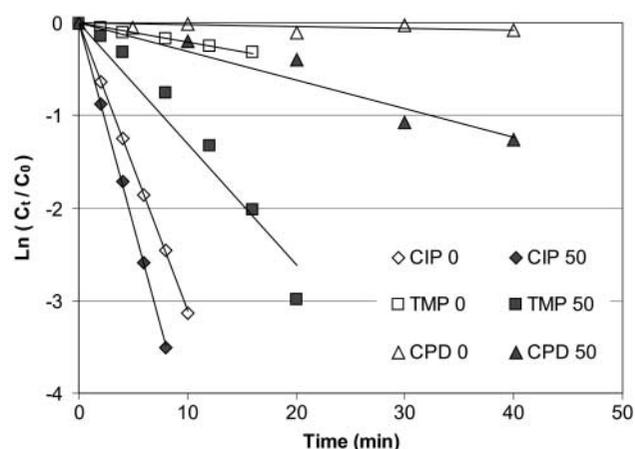


Figure 1 | Degradation of CIP, TMP and CPD by UV/H₂O₂ vs. time using the CBA, in PBS (2.5 mM, pH 7), with and without addition of 50 mg/L H₂O₂. Numbers in the legends (0 and 50) refer to H₂O₂ concentration in mg/L.

are due to the magnitude of the compound's molar absorption coefficients and its overlap with the emission spectra of the UV lamp, as well as differences in the compounds quantum yields.

As expected, addition of 50 mg/L H₂O₂ to the photolysis process increased the degradation rate of all examined compounds, thus, the combined UV/H₂O₂ process is more effective than UV alone, presumably due to [•]OH radical formation. Degradation of CPD in the UV/H₂O₂ process was previously examined by Kim *et al.* (2009). Their study showed that addition of 6 mg/L H₂O₂ to the photolysis process in pure water (using monochromatic UV lamp at 254 nm) increased the CPD degradation rate constant by factor of 12. For comparison, in the present study, addition of 50 mg/L H₂O₂ to the photolysis process of CPD increased its degradation rate constant by a factor of ~90.

H₂O₂ concentration is an important operating parameter in the UV/H₂O₂ process. Figure 2 presents the UV/H₂O₂ time based degradation rate constants (k_{app} , 1/min) of the studied compounds as a function of H₂O₂ initial concentration, in the range of 0–200 mg/L. The degradation rate of

Table 1 | Measured rate constants for the examined pharmaceuticals

	[•] OH		O ₃			
	Method	Measured $k_{OH,C}$ (1/M s)	Literature $k_{OH,C}$ (1/M s)	Method	Measured $k_{O3,C}$ (1/M s)	Literature $k_{O3,C}$ (1/M s)
CIP	CK mod. ^a	5.0×10^9	4.1×10^{9c}	CK ^b	2.2×10^4	1.9×10^{4c}
TMP	CK ^b	6.4×10^9	6.9×10^{9c}	CK ^b	4.5×10^5	2.7×10^{5c}
CPD	CK ^b	1.3×10^9	2×10^{9d}	O ₃ in excess	2.5	3.3^d

^aCompetition kinetic modified for direct photolysis (Equation (3)).

^bCompetition kinetic.

^cDodd *et al.* (2006).

^dGarcia-Ac *et al.* (2010).

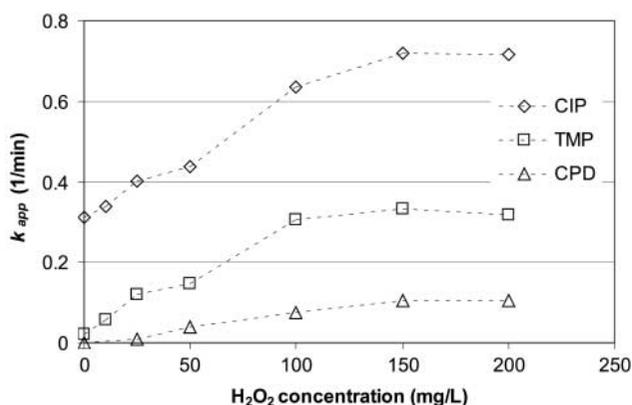


Figure 2 | UV/H₂O₂ time based degradation rate constants (k_{app}) of CIP, TMP and CPD, in PBS (2.5 mM, pH 7), at different initial H₂O₂ concentrations.

CIP, CPD and TMP with UV was steadily increased with addition of H₂O₂ at concentrations up to 150 mg/L. However, further increase in H₂O₂ concentration above 150 mg/L, did not improve the degradation rate of the selected compounds. The tailing observed at H₂O₂ concentrations higher than 150 mg/L is a well-documented phenomenon (e.g. Aleboye *et al.* 2004; Lester *et al.* 2010) and can be explained by the H₂O₂ scavenging effect on \cdot OH and by the pharmaceuticals UV light screening due to H₂O₂ light absorbance, both occur predominantly at high H₂O₂ concentration. As a control experiment, the impact of H₂O₂ alone was evaluated on the degradation of CIP, TMP and CPD (without UV light). No degradation of the compounds was observed when H₂O₂ was used at concentration of 200 mg/L and contact times up to 48 h.

\cdot OH radicals were previously indirectly quantified using the *p*CBA method (Lester *et al.* 2010). These results indicate a steady increase in \cdot OH radical concentration from 2.9×10^{-14} to 4.7×10^{-13} M when increasing H₂O₂ initial concentration from 10 to 150 mg/L. A further increase in H₂O₂ concentration to 200 mg/L had almost no effect on \cdot OH concentration (i.e. 4.8×10^{-13} M).

Pharmaceutical degradation by UV/H₂O₂/O₃

In the UV/H₂O₂/O₃ treatment, \cdot OH radicals are generated through several different processes where each can operate as an independent AOP (Glaze *et al.* 1987), namely: (a) O₃ reaction with OH⁻, (b) UV photolysis of H₂O₂, (c) the combined application of ozone and hydrogen peroxide and (c) UV photolysis of ozone, generating \cdot OH through a sequence of reactions, initiated by the formation of H₂O₂. In addition, direct degradation of the target pollutant may occur by UV photolysis and direct oxidation by ozone. In order to

better understand the UV/H₂O₂/O₃ mechanism, each of the above processes was examined separately.

Degradation by O₃ based processes

Figure 3 illustrates the degradation of the pharmaceuticals in the ozone process, for different initial dissolved ozone concentrations (0.1–1 mg/L). Results for TMP were not plotted, as TMP completely degraded at the lowest ozone concentration of 0.1 mg/L, in less than 1 min. In all cases, a first order kinetic was observed, up to 30 min. For both CIP and CPD, degradation rate increased with an increase in initial ozone concentration. CPD showed the slowest degradation rate, at any ozone concentration, while TMP degraded the fastest. The observed degradation rates correlate well with the compound's calculated rate constants with O₃ and \cdot OH, as presented in Table 1. Previous studies have already demonstrated the low O₃ degradability of CPD (Kim *et al.* 2008) and the quick reaction of TMP and CIP with O₃ (Dodd *et al.* 2006).

Addition of H₂O₂ to the ozone process creates AOP conditions and may enhance the degradation of the pharmaceuticals. Table 2 presents the pseudo-first order time-based degradation rate constants of CIP and CPD, by the H₂O₂/O₃ process ($[O_3]_0 = 0.5$ mg/L), without H₂O₂ and with the addition of H₂O₂ at concentrations 0.17 and 0.35 mg/L. Results for TMP were not presented due to immediate O₃ degradation, as stated above. The degradation rate of CPD steadily increased with increase in H₂O₂ concentration, while the degradation rate of CIP increased at low concentration of H₂O₂ but decreased at the higher H₂O₂ level. CIP reacts relatively fast with molecular O₃ ($k_{O_3,CIP} = 2.2 \times 10^4$), therefore, H₂O₂ which competes with CIP over

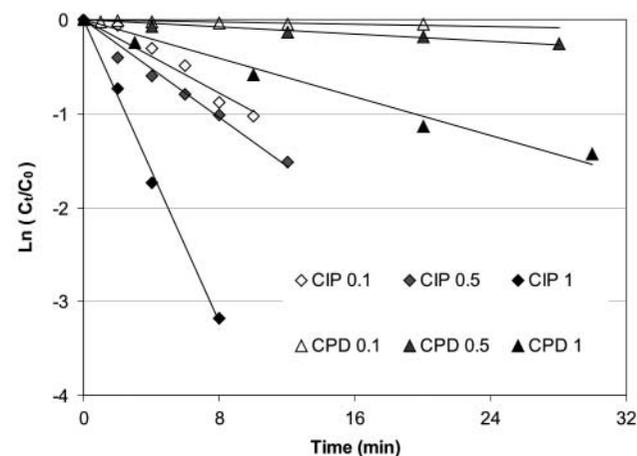


Figure 3 | Degradation of CIP and CPD with time at different initial dissolved O₃ concentrations in PBS (1 mM, pH 7). Numbers in the legends refer to O₃ concentration in mg/L.

Table 2 | H₂O₂/O₃ time-based degradation rate constant (k_{app} , 1/min) of CIP and CPD at different H₂O₂ initial concentrations. Initial O₃ dissolved concentration 0.5 mg/L

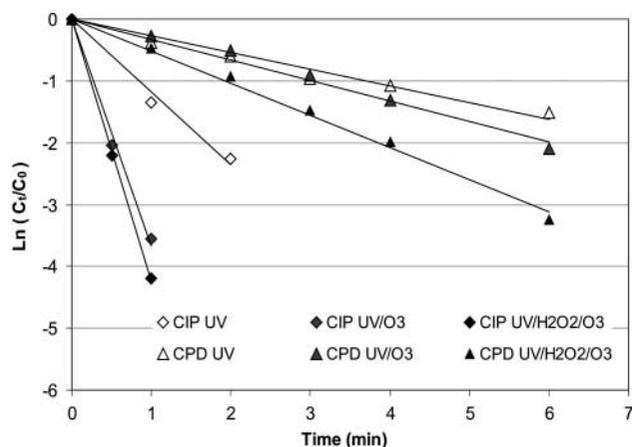
H ₂ O ₂ concentration (mg/L)	0	0.17	0.35
CIP	0.113	0.171	0.121
CPD	0.008	0.0164	0.0227

O₃, may ultimately reduce its degradation rate. For CPD, direct reaction with O₃ is negligible, thus increasing H₂O₂ concentration (within the tested range) will increase [•]OH formation, resulting in a higher degradation rate of CPD.

Kim *et al.* (2008) found that the addition of 2.3 mg/L H₂O₂ to the O₃ process slightly improved the degradation rate of CPD, while De Witte *et al.* (2009) reported an improvement in degradation rate of CIP from water by O₃ with the addition of up to 1.7 mg/L H₂O₂. Contrarily, Vasconcelos *et al.* (2009a) found that the H₂O₂/O₃ process was slower than O₃ alone for the removal of CIP from wastewater effluent. Their results may be explained not only by the fast direct reaction of CIP with O₃, but also by the scavenging effect of constituents in the wastewater effluent on [•]OH radicals.

Degradation by UV based processes

Time based degradation of CIP and CPD by the UV, UV/O₃ and UV/H₂O₂/O₃ processes (in the 1 L batch reactor) are presented in Figure 4. Initial concentration of dissolved O₃ (before pollutant's injection) was 0.5 mg/L (for UV/O₃ and UV/H₂O₂/O₃) and initial H₂O₂ concentration was 2 mg/L (for UV/H₂O₂/O₃). At conditions studied, direct UV showed the slowest degradation rate for both compounds. For CPD, degradation rate decreased as follow: UV/H₂O₂/O₃ > UV/O₃ > UV. While for CIP the UV/O₃

**Figure 4** | Degradation of CPD and CIP with time by the UV, UV/O₃ and UV/H₂O₂/O₃ processes in PBS (2.5 mM, pH 7) ([O₃]₀ = 0.5 mg/L; [H₂O₂]₀ = 2 mg/L).

and UV/H₂O₂/O₃ processes showed almost similar degradation rate, thus the addition of H₂O₂ to the UV/O₃ process have practically no additional value on the degradation rate of CIP.

Wang *et al.* (2005) studied the impact of different AOPs on the degradation of three chlorophenols found in a Kraft-pulp bleach plant effluent. Their study showed that degradation efficacy of each AOP was compound dependent. For example the addition of H₂O₂ to an UV/O₃ system improved the degradation rate of 2, 3, 4, 5-Tetrachlorophenol and had no effect on the degradation of 4, 5-Dichloroguaiacol. Kusic *et al.* (2006) found that phenol decay was similar in the UV/O₃ and UV/H₂O₂/O₃ processes; however, UV/H₂O₂/O₃ achieved higher mineralization (i.e. TOC removal). Thus, the UV/H₂O₂/O₃ process may have an advantage over other AOPs in the degradation of specific (i.e. refractory) target compounds, as well as in their mineralization. Complete mineralization of the target pollutant is advantageous due to possible unwanted formation of active intermediate byproducts resulting from the degradation of the parent compound.

Electrical energy efficiency

The electrical-energy per order parameter (E_{EO}) was determined, as the studied degradation processes are electrical energy related processes. The E_{EO} parameter corresponds to the amount of electrical energy (kWh) required to reduce one order of magnitude (90% removal of contaminant) in a treated volume of contaminated water (Bolton *et al.* 2001).

$$E_{EO} = \frac{P}{26.1 \times V \times k_{app}} \quad (4)$$

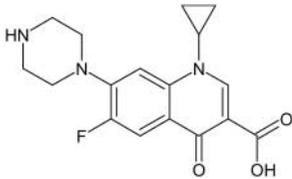
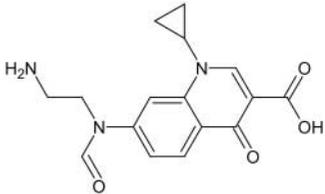
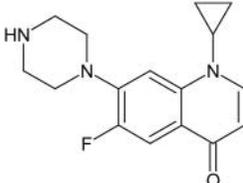
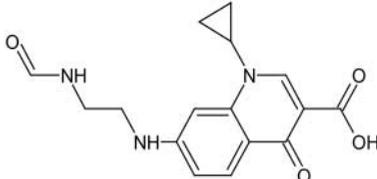
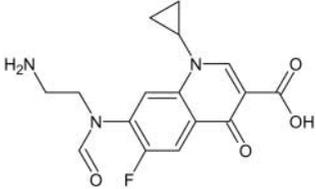
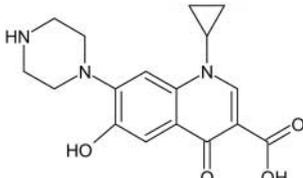
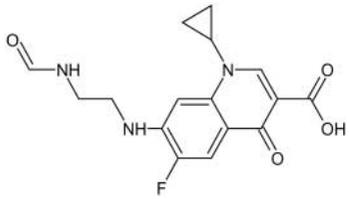
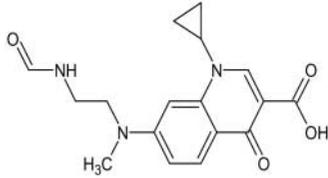
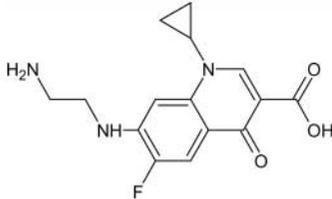
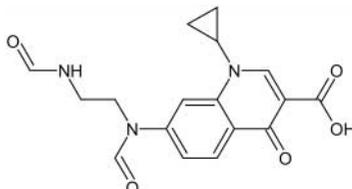
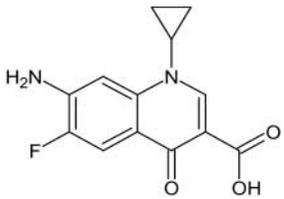
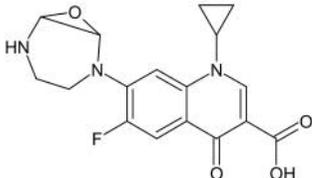
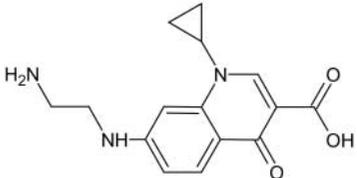
where, P is the rated power of the system (kW), V is the total volume of water treated (m³) and k_{app} is the time-based degradation rate constant of the examined compound (1/min).

The rated power was calculated as the sum of the UV lamp power (0.45 kW), the O₃ production power and the energy cost of H₂O₂. Where, the O₃ production power

Table 3 | E_{EO} values (kWh/m³/order) of CIP and CPD at different processes

	UV	UV/O ₃	UV/H ₂ O ₂ /O ₃	O ₃	H ₂ O ₂ /O ₃
CIP	16.3	5.2	5.1	3.2	2.2
CPD	70.7	59.1	37.8	19.7	7.2

Table 4 | HPLC/MS analysis of CIP direct UV degradation byproducts

No. (m/z)	Rt ^a	Proposed product structures	No. (m/z)	Rt ^a	Proposed product structures
CIP 332.1	4.9				
1 (316.1)	2.9		7 (288.1)	7.0	
2 (316.1)	6.1		8 (334.1)	3.4	
3 (330.1)	2.8		9 (334.1)	6.8	
4 (330.1)	7		10 (306.1)	4.0	
5 (344.1)	5.5		11 (263.1)	7.5	
6 (346.1)	4.4		12 (288.1)	3.2	

^aMS retention time (min).

was based on the product of the measured current and voltage of the ozone generator and the energy cost of H₂O₂ was calculated as the ratio between the local costs of H₂O₂ (\$/mg) and electricity (\$/kWh). It should be noted however that at the examined H₂O₂ range it had only minor contribution to the E_{EO} value. E_{EO} results for CIP and CPD in the 1 L batch reactor, for each of the examined process, are presented in Table 3. For the O₃ based process E_{EO} was calculated for initial O₃ concentration of 0.5 mg/L. For the H₂O₂/O₃ process E_{EO} was calculated for initial H₂O₂ concentration of 0.17 and 0.35 mg/L for CIP and CPD respectively.

From Table 3 it can be concluded that for the studied compounds and operating parameters, the O₃ based processes (i.e. O₃ and H₂O₂/O₃) consume less electrical energy than the processes where UV light was used. The electrical energy consumption for CPD was in the following order: UV > UV/O₃ > UV/H₂O₂/O₃ > O₃ > H₂O₂/O₃, while for CIP E_{EO} was similar for UV/O₃ and UV/H₂O₂/O₃, thus, the most energy-efficient process was the combination H₂O₂/O₃. Earlier studies have confirmed the advantage of O₃ based processes over UV based processes in terms of energy efficiency (e.g. Muller & Jekel 2001).

Photo-degradation intermediates analysis

The formation of intermediate byproducts, following the degradation of an organic pollutant by UV or O₃ based processes, is one of the most important issues in the field of pharmaceutical removal. Active degradation intermediates may occasionally be formed, in particular if the active part of the molecule remains unmodified. The importance of this topic is demonstrated in Table 4, where 12 byproducts, identified during direct UV photolysis of CIP, are presented. The moieties which are involved in the CIP photo-degradation are the piperazine residue, the carboxylic group and the fluorine atom. The quinolone skeleton however remains unchanged. The piperazine ring is either subjected to breakdown (intermediates 1–2, 4–5 and 8–12) or is epoxidized at positions 2, 3 (of the piperazine). Decarboxylation occurs at position 3 of the quinolone skeleton (intermediate 7). The fluorine at position 6 is either substituted by hydroxyl group (intermediate 3) or by hydrogen atom (intermediates 1, 2, 4, 5 and 12). In light of the fact that the characteristic quinolone is believed to be responsible for the CIP antimicrobial activity (Dodd *et al.* 2006), intermediates which merely involve modification of the piperazine

residue may still potentially exhibit antibacterial potencies. Various researchers have already identified the formation of different byproducts as a result of CIP photo-degradation (e.g. Vasconcelos *et al.* 2009a).

CONCLUSIONS

AOPs which combine UV photolysis, hydrogen peroxide and ozone may present an attractive treatment for the degradation of a wide range of pharmaceuticals in water. Out of the examined processes, O₃ had the highest degradation rate for TMP and H₂O₂/O₃ showed highest degradation rate for CIP and CPD. H₂O₂ concentration was found to be an important parameter in the UV/H₂O₂ and H₂O₂/O₃ sub-processes, acting as an [•]OH initiator at low concentrations and as an [•]OH radical scavenger at higher concentrations. The electrical energy consumption, as calculated using the E_{EO} parameter, showed that O₃ based processes were more efficient than UV based processes, where O₃ was the most efficient process for the degradation of TMP, and H₂O₂/O₃ was the most efficient process for the degradation of CIP and CPD. Twelve degradation byproducts were identified following direct UV photolysis of CIP. Future research will investigate the formation of degradation byproducts for CIP, CPD and TMP under the different AOP conditions and evaluate their potential toxicity.

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